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MEASURING THE SOLIDS CONTENT OF HONEY AND OF STRAWBERRY JAM WITH A HAND REFRACTOMETER[1]

BY JESSE A. PEARCE[2] AND SUZANNE JEGARD[2]

Abstract

A hand refractometer may be useful for routine inspection of the solids content of honey, and of strawberry jam containing added pectin. For 76 pairs of determinations on honey,

$$y = 1.116x - 7.58,$$

with a standard error of prediction of $\pm 0.4\%$; for 116 pairs of determinations on the jam,

$$y = 1.022x - 0.79,$$

with a standard error of prediction of $\pm 0.3\%$, where y is the per cent solids by the A.O.A.C. vacuum-oven method and x is the reading on the hand refractometer. A standard error of $\pm 0.5\%$ was observed for determinations by the vacuum-oven method, and of $\pm 0.4\%$ for determinations with the hand refractometer.

Introduction

The solids content of products such as honey and jam can be readily determined by the vacuum-oven method (1, p. 582) or with an Abbé refractometer (2). While neither method is suitable for field inspection, determinations using a hydrometer (3) have been reasonably satisfactory for inspection work. Since relatively inexpensive hand refractometers have provided a simple and rapid method of determining egg solids under field conditions (4), these laboratories were asked to calibrate a hand refractometer in terms of the solids content of honey, and of strawberry jam containing added pectin. This paper describes these calibrations.

The Hand Refractometer

The hand refractometer used in this work was manufactured by the Bausch and Lomb Optical Company, Rochester, New York. It is calibrated for sucrose solutions containing from 40 to 85% solids, and the scale can be read within $\pm 0.2\%$ at solids contents of about 40% and within $\pm 0.1\%$ at 80%. The refractometer is designed for use at 68° F. (20° C.) and has a correction thermometer attached, which is calibrated in per cent sucrose according to the temperature coefficient for the refractive index of sucrose solutions.

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Application to Honey

Since the temperature coefficient for the refractive index of sucrose solutions differs slightly from that for honey (0.00018 and 0.00023 respectively per degree Centigrade), readings on honeys of different solids content were compared at temperatures of 40°, 60°, 80°, and 100° F. (4°, 16°, 27°, and 38° C.). Table I shows that the correction thermometer on the instrument can be used with reasonable accuracy over this temperature range; but that vague lines, dividing the light and dark fields in the refractometer, interfered with the

TABLE I

VARIATION IN HAND REFRACTOMETER READINGS, %, WITH TEMPERATURE OF HONEY

Sample	Solids, at various temperatures, °F.			
	40	60	80	100♀
1	♀♀	♀♀	♀♀	86.1
2	♀♀	♀♀	86.4	86.1
3	♀♀	85.0	85.0	84.8
4	♀♀	84.3	84.2	84.1
5	♀♀	83.8	83.8	83.6
6	82.0	82.1	82.1	81.9
7	81.4	81.6	81.3	81.4
8	79.1	79.1	79.0	79.1
9	78.6	79.5	79.3	77.7
10	77.0	77.2	77.1	77.2
11	76.7	76.7	76.4	76.6

♀ *Readings difficult, double line formed in refractometer.*
♀♀ *Line in refractometer too vague to permit a valid reading.*

measurement at 100° F. Temperatures between about 60° and 80° F. gave the best results and all further measurements on honey were made within these limits.

Vague lines observed for concentrated honeys held at low temperatures were attributed to partial crystallization of the sugars. Comparative measurements on samples of fluid and crystalline honeys containing 75 to 80% solids showed that crystallized honey gave hazy lines in the refractometer and could not be used for this test. All further work was done on fluid honey.

Tables relating solids content of honey by the A.O.A.C. vacuum-oven method and refractive index on an Abbé refractometer have been published (2). These data were converted to readings on the hand refractometer at 68° F. to give the curve shown in Fig. 1. Honey was diluted to give a range of solids from 76 to 88%, determined by the vacuum-oven method, and the mixtures were examined in the hand refractometer. The results are given as points on Fig. 1; they show close agreement between the previous and present techniques, and support the use of the hand refractometer.

To assess the application of this instrument, the solids in 76 samples of honey obtained in routine inspections were determined by the vacuum-oven method and with the hand refractometer. The samples were obtained during

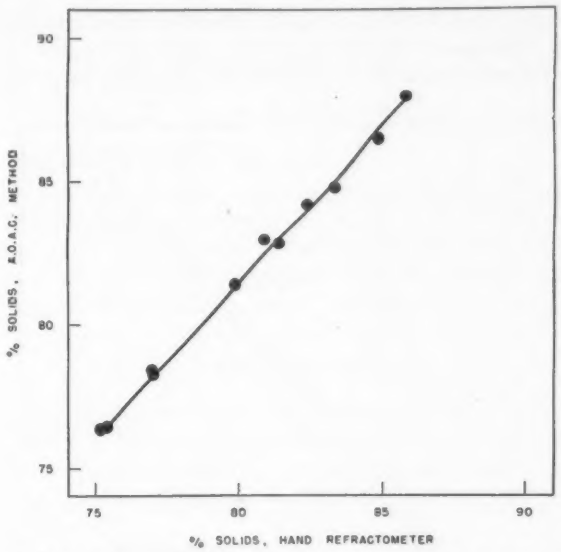

FIG. 1. *Relation between solids in honey as determined by the A.O.A.C. vacuum-oven method and by the hand refractometer.*
Solid line—values converted from refractive indices in Ref. (2).
Points—values determined in course of present study.

1946 and 1947 from all Canadian provinces but New Brunswick and Prince Edward Island and were classed as white, golden, light amber, dark amber, and dark. Statistical analysis showed that, in general, the color of the honey and the year of production had little effect on the measurement, but that honey of the same color from different provinces gave equations that were significantly different. For example, the regression lines for golden honey from different provinces, shown in Fig. 2, are statistically different, but the maximum difference between the curves is about the same order as the standard error ($\pm 0.4\%$) of an equation for 76 samples,

$$y = 1.116x - 7.58$$

where y is the per cent solids by the vacuum-oven method and x is the hand refractometer reading.

Application to Strawberry Jam Containing Added Pectin

The solids in fluid honey can be determined without preliminary separation, but the solids in jams are usually determined on a separated fluid that is as free as possible from suspended matter. In this work, separation was effected

by straining juice from the jam through muslin bolting cloth No. 12XX (1, p. 381). The solids in the strained liquid were determined by the hand refractometer, and by the A.O.A.C. vacuum-oven procedure (1, p. 556), but using sand in the moisture tins (1, p. 557).

Although the solid material in fluid separated from jam is primarily sucrose, the correction thermometer on the hand refractometer was checked by readings on four jams, ranging in solids from 62 to 71%, at temperatures of 40°, 60°,

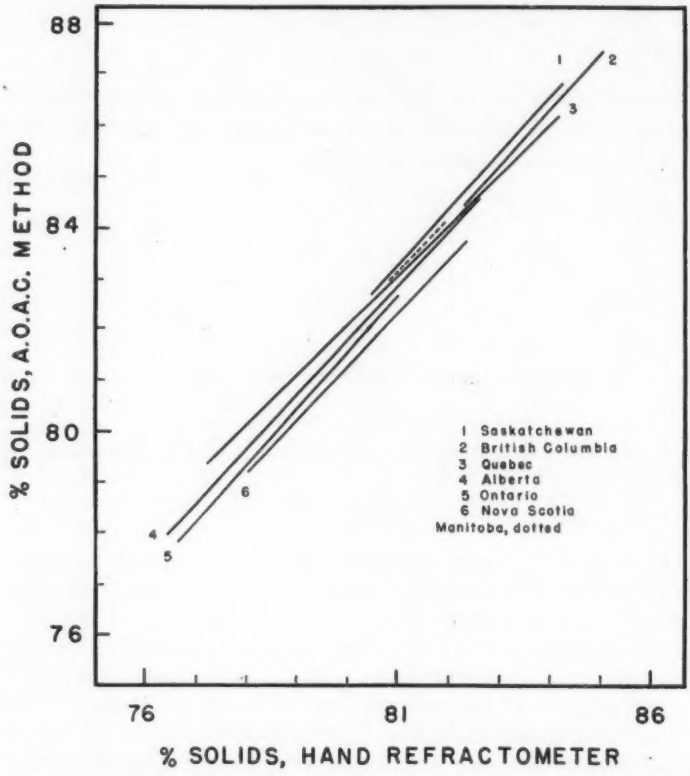

FIG. 2. *Relation between solids in golden honeys, by provinces, as determined by A.O.A.C. vacuum-oven method and by the hand refractometer.*

80°, and 100° F. The averages were 66.8, 66.6, 66.3, and 67.0% at the four respective temperatures, with a necessary difference of 0.4%*. Consequently, a temperature range from 60° to 80° F. is recommended when using the hand refractometer for inspection work.

To determine the error in either method and the relation between the two methods of measurement, 29 one-pound samples of strawberry jam with added

* *Five per cent level of statistical significance.*

pectin were collected during routine inspections, and each sample was divided into four parts, which were placed in sealed containers. Single measurements of the solids content were made on different days on each part of each sample by both techniques.

For the 116 pairs of measurements on these jams, which ranged from 61% to 72% in solids, the relation between the per cent solids by vacuum-oven method (y) and the hand refractometer reading (x) was

$$y = 1.022x - 0.79,$$

with a standard error of prediction of $\pm 0.3\%$.

The vacuum-oven method, which is usually considered to be the reference method, had no greater accuracy than the hand refractometer. An examination of the data for jams showed that solids contents were determinable by the vacuum-oven method with a standard error of $\pm 0.5\%$, and by the hand refractometer with a standard error of $\pm 0.4\%$.

Acknowledgments

The authors wish to express their thanks to Mr. F. R. Armstrong and Mr. F. J. Perry of Marketing Service, Dominion Department of Agriculture, who kindly arranged for collection of the various samples; and to Dr. J. W. Hopkins, Statistician, Division of Applied Biology, for advice during the course of this work.

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THE FLUIDIZATION TECHNIQUE APPLIED TO DIRECT DISTILLATION OF OIL FROM BITUMINOUS SAND[1]

By P. E. Gishler[2]

Abstract

The fluidized solids technique has been applied successfully to the flash distillation of oil from Alberta bituminous sand on a laboratory scale. At 500° C. a 76% oil recovery was obtained. The remaining 24% produced approximately equal weights of coke and gaseous compounds. At temperatures below 460° C. trouble was experienced in maintaining a fluidized bed because of the slow rate of distillation. As temperatures were increased above 500° C. the yield of oil decreased, with a corresponding increase in gas formation.

Introduction

The use of a fluidized solids bed as a process tool is expanding rapidly. Its chief value lies in its applicability to reactions where a uniform temperature and good heat transfer are required. In reactions requiring a catalyst, a tremendous surface area under controlled conditions is made available.

The first extensive application has been in the catalytic cracking of oil (7). Here, the catalyst, in a finely divided state, forms the fluidized solids bed. The oil vapor to be cracked serves as the fluidizing agent. Another application has been in the calcining of limestone where the combustion gases fluidize the bed of lime (1), oil being fired directly into the fluidized bed. Recently, work has been published on its use in the distillation of oil from oil shale (8). Shale is a rocklike material that can be crushed and sized and in this respect it differs from Alberta bituminous sand, which consists of sand particles coated by a film of viscous bituminous oil. This exists in more or less firmly compacted beds of tremendous extent and considerable depth in an area bordering the Athabaska River in northern Alberta (5). Recently, an unusually rich deposit has been outlined in the Mildred Ruth Lake area (6).

There have been a number of attempts at developing equipment that would recover the oil content of these sands by distillation methods (5). These have failed, owing mainly to the difficulties resulting from the sticky nature of the bituminous sand and its extremely low heat transfer coefficient. In a more successful approach to the recovery of oil from bituminous sand, hot water has been used as the separating medium. This method of separation, with different modifications, has been studied extensively, both on a laboratory and semicommercial scale. Comprehensive reviews have been published (2, 3, 4, 5).

Fluidization

The fluidization technique has made it possible to carry out certain operations that would meet with difficulties in other conventional forms of apparatus.

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[2] *Chemist.*

A number of preliminary tests were therefore carried out in order to determine whether this technique could be successfully applied to the direct distillation of oil from Alberta bituminous sand.

The first experimental fluidizing unit was simply a 2 in. glass tube, 2 ft. long, drawn to a cone at the bottom end and open at the top. This was wound with resistance wire and insulated, except for a narrow area at the front and back, which served as a window. A 6 in. depth of sand constituted the fluidizing bed. A stream of preheated nitrogen was passed upwards through the bed in an amount sufficient to keep the bed in vigorous agitation. Tests were carried out in the temperature range 400° to 500° C.

The object was to gain information on the rapidity with which the oil could be distilled from the bituminous sand and to study the behavior of lumps of bituminous sand of varying size and compactness when they were dropped into the hot fluidized bed. The following information was gained:

(i) At 500° C. distillation was rapid. Heavy oil fumes were swept by the nitrogen stream out of the unit as soon as a lump was dropped into the bed, and fuming was completed in several seconds. The lumps, ranging in diameter from $\frac{1}{8}$ in. to 1 in., appeared to disintegrate to individual sand grains immediately on entering the bed. Each grain was coated with a thin closely adhering film of coke.

(ii) At 400° C. distillation was slower and the lumps fed to the still did not disintegrate as readily as at the higher temperature. Trouble was experienced with agglomeration.

The results of these preliminary tests indicated that the problems of heat transfer and handling encountered in other types of direct distillation apparatus could be overcome in a fluidized bed. Apparatus was therefore built to permit a quantitative study of direct distillation by this method. This might be considered as one step in a two step method of oil production consisting of:

(i) Flash distillation of oil in a fluidized bed,

(ii) Burning of the coke from the residual sand to generate the necessary heat for the distillation step.

Experimental

The work reported here consisted of a series of direct distillations of bituminous sand carried out at different temperatures. The yields of oil, coke, and gas were determined. The following analyses were carried out on the oil: distillation, density, viscosity, and total sulphur.

The apparatus is shown in Fig. 1. It consisted of a cylinder of nitrogen, which served as the fluidizing gas, a nitrogen preheater, a still containing a fluidized sand bed, a trap, an electrical precipitator, and an activated charcoal tower with auxiliary steaming equipment.

The still consisted of a stainless steel tube 3 ft. long and 2.5 in. in diameter, with a perforated plate 2.5 in. from the bottom to hold the charge and distribute the preheated nitrogen. A 1 in. tube welded to the plate served to draw

off the spent sand. Four thermocouples were placed as indicated. Three separate resistance coils surrounding the still supplied the required heat. The water cooled trap cooled the offgases and prevented any surge of dust from

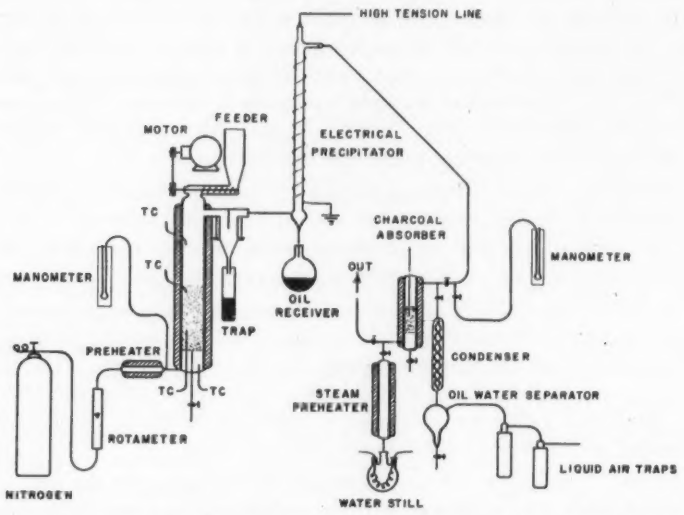

FIG. 1. *Apparatus for direct distillation of bituminous sand in a fluidized sand bed.*

reaching the remainder of the collection system. About one-third of the heavy oil and a small amount of carbon and fine dust were removed by the trap. The remainder of the heavy oil, which was in the form of a suspension in the offgas, was effectively removed by the electrical precipitator. The activated charcoal scrubber removed the light oil (mainly gasoline) and a part of the hydrocarbon gas fraction. This was recovered by steam distillation.

At the start of a run sufficient spent sand from a previous run was poured into the still to form a bed depth of 6 in. Nitrogen preheated to the distillation temperature was introduced at a rate sufficient to fluidize the bed. Gas rates were measured by means of a rotameter. The heaters were turned on and when the desired temperature was reached bituminous sand was fed continuously into the bed from a worm feeder. A charge of about 3000 gm. was used for each run. The spent sand bed was allowed to build up to 10 in. and maintained there by periodic removal through the 1 in. tube. This flowed freely from the system when the gate valve on the tube was opened. The behavior and depth of the bed could be determined by observing the manometer indicated in Fig. 1. Feed rates were 2000 to 2500 gm. per hr., the lower rates being necessary at the lower temperatures.

At the completion of a run the heavy oil was collected and measured. The light oil was steam distilled from the charcoal. The volatile fraction was caught in two liquid air traps placed in series.

Results

The bituminous sand used for these tests had a bitumen content of 16%, which is higher than the average for the field. This was supplied by the Bureau of Mines and consisted of drill cores obtained from the Mildred Ruth Lake district near the Athabaska River in Alberta. This material, although mined about one year ago, had a fresh, unweathered appearance.

Tests have also been made on freshly mined coarse bituminous sand from the Bitumount area and on fine, badly weathered sand from near Waterways. The results indicate that percentage recovery of oil does not vary appreciably with variation in the physical condition or oil content of the sand.

The results showing the influence of temperature on yields and physical properties are shown in Table I and Fig. 2. Yields are expressed as cubic centimeters of oil recovered per 100 cc. bitumen content in the bituminous sand feed.

TABLE I

INFLUENCE OF TEMPERATURE ON OIL RECOVERY

Run No.	16	15	13	10	17	11	14	12	18
Temperature, °C.	425	450	460	475	500	525	565	600	700
Bitumen in feed, cc.	100	100	100	100	100	100	100	100	100
Recovery heavy oil, cc.	62	68	74	71	73	63	52	33	21
Recovery light oil, cc.	2	2	2	3	3	6	9	10	10
Oil yield, vol. %	64	70	76	74	76	69	61	43	31
Coke in sand, wt. %	—	2.0*	2.0	2.0	1.9	1.8	1.8	1.7	3.3
Heavy oil analysis									
Specific gravity, 60° F./60° F.	.965	.975	.967	.971	.975	.978	.992	1.058	1.158
Viscosity, centistokes,									
100° F.	133	249	101	137	135	66	43	41	—
32° F.	6018	11300	2779	4254	4253	1381	699	902	—
Sulphur, %	4.03	4.41	3.91	3.88	3.86	4.08	4.29	5.00	3.13

* *Coke determined on free flowing sand only, lumps screened out.*

Highest yields were obtained in the temperature range 460° to 500° C. At lower temperatures, distillation was incomplete and a properly fluidized bed was difficult to maintain owing to lumping up of the charge. Above 500° C., cracking became progressively more severe, resulting in increased formation of light oil and gas. A temperature of 500° C. may be considered as the

optimum when both ease of operation and yield are considered. Expressed in terms of bituminous sand of 16% bitumen content, 1 ton of bituminous sand will produce 0.7 bbl. of oil, free of water and solids.

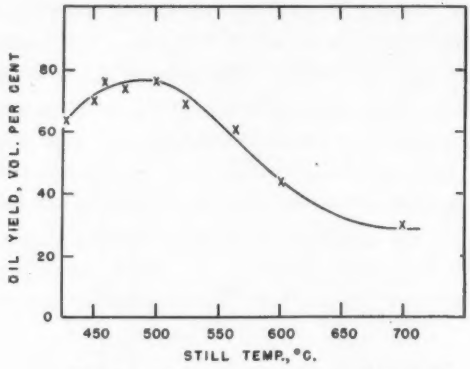

FIG. 2. *Oil recovered from bituminous sand.*

The oil had a high specific gravity, was quite fluid at room temperature, and was high in sulphur. Suspended solids amounted to 0.1% by weight. Distillation data are given in Table II.

TABLE II

DISTILLATION OF HEAVY OIL PRODUCED IN FLUID STILL

Run No.	16	15	13	10	17	11	14
Initial boiling point, °F.	382	415	290	380	373	300	259
5% recovered, °F.	513	523	464	499	474	426	405
10% "	549	558	533	553	537	603	464
20% "	587	602	599	594	591	564	529
30% "	623	619	628	614*	613	562*	590
40% "	637	614	640	606	626		613
50% "	647	612*	647	594	622*		613*

* *Evidence of cracking.*

A sample of heavy oil produced in a run at 500° C., using bituminous sand from Bitumount, 55 miles north of Waterways, was distilled at 10 mm. pressure. The data corrected to atmospheric pressure are given in Table III.

TABLE III

DISTILLATION OF HEAVY OIL AT LOW PRESSURE (CORRECTED TO 760 MM.)

5% – 442° F.	40% – 676° F.
10% – 498	50% – 745
20% – 568	55% – 752
30% – 617	

Two light oil samples were accumulated. Sample 1 included runs at 500° C. and lower. Sample 2 included runs at 565° C., 600° C., and 700° C. Distillation data are shown in Table IV.

TABLE IV

DISTILLATION OF LIGHT OIL

Distillation	Sample 1	Sample 2
Initial boiling point, °F.	97	86
5% recovered, °F.	104	91
10% "	117	131
20% "	151	163
30% "	181	183
40% "	201	201
50% "	217	217
60% "	235	234
70% "	255	250
80% "	279	273
90% "	324	338

Gas Formation

Aside from the gasoline fraction, the activated charcoal also removed the heavier gaseous hydrocarbons formed by cracking. On steam distilling of the charcoal, these were caught in two liquid air cooled traps. The volumes recovered, however, could not be used to determine gas production quantitatively because the efficiency of the charcoal absorber was not known. To determine gas yields the following apparatus was therefore set up (Fig. 3).

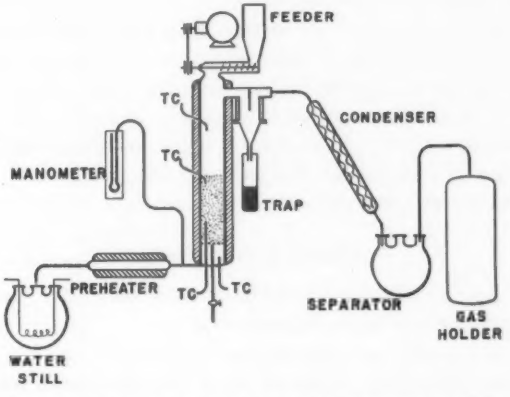

FIG. 3. *Apparatus to determine yield of gaseous products.*

Steam was used as the fluidizing gas. This was produced at known rates in an electrically heated steam generator. The steam preheater, still, and trap were the same as used for the experiments described above. The trap and a large water cooled condenser removed the steam and the bulk of the oil. The light hydrocarbons and hydrogen passed through to a gasometer, where their volume was measured. Bituminous sand was fed at a known rate into the still so that gas production could be determined quantitatively. The temperature range 465° to 600° C. was studied. The results are shown in Fig. 4.

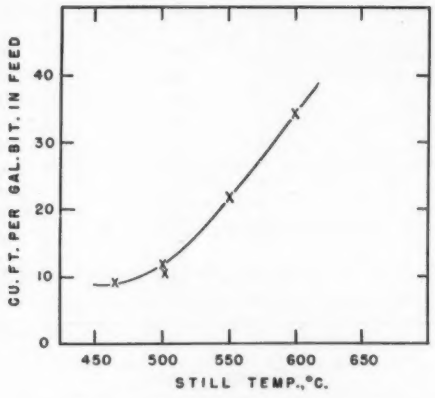

FIG. 4. *Gas formation due to cracking.*

Accurate and complete analyses of the gases were impossible under the conditions of the experiments, owing to high sulphide gas content. On a Burrell gas analysis apparatus, results varied considerably. These indicated, however, that the amounts of saturated and unsaturated hydrocarbons were about equal, amounting to approximately 40% each on a sulphide free basis. The hydrogen content was approximately 15%.

The above described method of producing a petroleum distillate by direct flashing of oil from tar sands is believed to be a simplified approach to the problem of utilization of the bituminous sand deposits. The data presented, however, cannot be used to determine capacities or costs. These must await pilot scale operation data. A search of the literature would indicate that further data are also required on the various other methods of extraction that are under study, before a comparative analysis can be made.

Acknowledgment

Thanks are due to Mr. A. Lafortune and Mr. Neil Scheel for their assistance in carrying out these experiments.

The author also wishes to acknowledge with thanks the co-operation of the Bureau of Mines and of Dr. K. A. Clark of the Research Council of Alberta for supplying bituminous sand samples.

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THE WEATHERING CHARACTERISTICS AND ROT RESISTANCE OF COTTON DUCK TREATED WITH THE COPPER COMPLEX OF NITROSOPHENYLHYDROXYLAMINE[1]

By C. H. Bayley[2] and Muriel W. Weatherburn[2]

Abstract

Unbleached cotton tentage duck treated with the copper and copper–iron complexes of nitrosophenylhydroxylamine showed considerable resistance to rotting in soil burial tests but gave evidence of enhanced actinic degradation and loss of treating compound as a result of outdoor weathering for three months during the summer. With samples containing a higher concentration of the complexes this degradation was more severe.

The efficacy of a number of organic compounds, capable of forming chelate copper complexes, in protecting cotton tentage duck from microbiological attack, has recently been examined by Illman and coworkers (5). In this work, in which resistance to microbiological attack was measured by noting the ability of the treated fabric to withstand deterioration during soil burial, it was found that the copper complex formed with ammonium nitrosophenylhydroxylamine ("Cupferron") conferred a high level of resistance. It has been shown previously (2) that the weathering characteristics of rot resistant treatments are of importance where the treated fabric is expected to withstand the effects of outdoor exposure. In this connection, the extent to which the treatment is removed by weathering, or tends to influence the actinic deterioration of the fabric, is of considerable importance in assessing the merit of a given treatment. It was therefore of interest to examine in some detail the weathering characteristics of the copper complex of nitrosophenylhydroxylamine when applied to cotton duck. This has been done for (*a*) two concentrations of the complex (Samples *A* and *D*), (*b*) a mixture of the complex and a standard cuprammonium treatment (Sample *B*), and (*c*) a mixture of the copper and iron complexes (Sample *C*). For purposes of comparison, the weathering characteristics of a sample of the duck carrying a standard cuprammonium treatment were also investigated (Sample *E*). The maximum copper content of the samples investigated was around 0.5% (Samples *A*, *B*, and *E*), since this content of copper is similar to that used in commercial treatments.

The samples were tested for rotproofness by the soil burial method before and after weathering by measuring the loss in breaking strength resulting from two and four weeks' burial. In addition, measurement was made of the loss of copper and of the increase in cuprammonium fluidity occurring during weathering.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1891.

[2] *Chemist.*

Materials Used

The fabric was an unbleached cotton tentage duck weighing 10 oz. per square yard, similar to that used in previous work (2). The Cupferron was obtained from Eastman Kodak Company. The copper acetate ($Cu(C_2 . H_3O_2)_2H_2O$), copper sulphate ($CuSO_4 . 5H_2O$), and ferric ammonium sulphate ($Fe_2(SO_4)_3 (NH_4)_2 . 24H_2O$) were of technical grade.

The fabric was wetted out in a 0.1% solution of technical sodium lauryl sulphate (Gardinol WA was used) and well rinsed in water. The treatment was then applied at room temperature by a two-bath process in which the fabric in the form of a loop was passed through an aqueous solution of Cupferron for 15 min. using the motor driven rubber covered rolls of a laundry wringer, and then through the solution of the metallic salt or mixture of salts for 15 min. The impregnated fabric was rinsed for two hours in running tap water and air dried. The copper contents of the treated fabric were determined as previously (3). It might be noted that the amount of copper fixed on the fabric by use of copper and iron salts plus Cupferron was considerably lower than that fixed by the same concentration of copper and iron salts plus soda ash, as used in another experiment (6).

Test Methods

The procedures for carrying out the leaching and burial treatments and for determining breaking strengths and cuprammonium fluidity were as previously used (1). The results of a statistical analysis of the breaking strength data indicated that for statistical significance at the 5% level with 10 breaks carried out on each sample, the necessary differences were as follows: leached samples, 17 lb.; weathered samples, 10 lb.; samples leached and buried four weeks, 21 lb.; samples weathered and buried two and four weeks, 16 lb. It was found that breaks occurring at the jaws of the machine gave lower and somewhat more erratic values than those occurring at some distance from the jaws; therefore "jaw breaks" were discarded and in those cases in which the full set of 10 breaks was not obtained, owing to jaw breaks, a formula described elsewhere (4) was used to determine the significant difference between the various sets of specimens.

The samples were exposed to outdoor weathering conditions on the roof of the National Research Laboratories, Ottawa, from 12th June to 12th September 1946.

Data

Table I gives the details of the treating solutions used and the copper contents and colors of the treated fabrics. Data for the weather conditions during the weathering period are given in Table II. The data for breaking strengths on weathering and on burial are given in Table III, and the increase in cuprammonium fluidity and decrease in copper content on weathering in Tables IV and V respectively.

TABLE I

CONCENTRATIONS OF TREATING SOLUTIONS AND CHARACTERISTICS OF TREATED FABRIC

Sample	Treatment		% copper on treated fabric	Color of treated fabric	
	Bath No. 1	Bath No. 2		Munsell notation*	I.S.C.C.–N.B.S. Name**
A	Cupferron 25 gm./liter	Copper acetate 20 gm./liter	0.44	6Y,7.7/1.6	Yellowish gray
B	Cupferron 25 gm./liter	Copper sulphate 100 gm./liter treated with ammonium hydroxide (28% NH_3) until blue precipitate just dissolved	0.52	10Y,7.7/2.5	Pale yellow green
C	Cupferron 25 gm./liter	Copper sulphate 87 gm./liter, ferric ammonium sulphate 93 gm./liter	0.13	1Y,7.6/3.5	Weak yellowish orange
D	Cupferron 5 gm./liter	Copper acetate 20 gm./liter	0.26	6Y,8/2	Weak yellow
E	Cuprammonium solution (as in Bath 2 of Treatment *B*)		0.57	8GY,8.2/1.0	Light greenish grey

* *Munsell Book of Color, Munsell Color Co. Inc., Baltimore, Md. (1942).*
** *Judd D. B. and Kelly K. L. J. Research, Natl. Bureau of Standards, 23, 355–385 (1939).*

TABLE II

WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

Period	Mean daily temp., °F.		Rainfall, in.	Bright sunshine, total hours
	Maximum	Minimum		
June 12 – June 15	68	47	0.02	48.6
16 – 22	74	51	3.49	62.3
23 – 29	91	62	0	83.7
30 – July 6	81	62	0.37	87.9
July 7 – 13	80	58	0.88	75.5
14 – 20	86	55	0.04	71.2
21 – 27	82	59	1.57	46.3
28 – Aug. 3	86	57	0.44	51.8
Aug. 4 – 10	91	59	2.25	67.1
11 – 17	79	62	0.11	46.4
18 – 24	77	52	1.10	26.5
25 – 31	77	48	0.44	38.4
Sept. 1 – Sept. 7	74	48	0.10	57.9
8 – 12	72	50	0.49	26.3
Average	80	55		
Total			11.30	789.9

TABLE III

EFFECT OF WEATHERING AND BURIAL ON BREAKING STRENGTH

Treatment	Breaking strength, lb.							Breaking strength loss, %					
	Orig. leached	*W* 3 mo.	Buried for 2 weeks after		Buried for 4 weeks after		Leached 24 hr. buried 8 wk.	*W* 3 mo.	Buried for 2 wk. after		Buried for 4 wk. after		*L* 24 hr. and buried 8 wk.
			L 24 hr.	*W* 3 mo.	*L* 24 hr.	*W* 3 mo.			*L* 24 hr.	*W* 3 mo.	*L* 24 hr.	*W* 3 mo.	
A. Cupferron (25 gm./liter soln.) + copper	164(9)	98(10)	166(4)•	90(10)	142(8)	0	44(3)•	40	+1	45	13	100	73
B. Cupferron (25 gm./liter soln.) + cuprammonium	162(10)	98(9)	163(3)•	94(10)	84(10)	10(9)	32(4)•	40	+1	42	48	94	80
C. Cupferron (25 gm./liter soln.) + copper + iron	161(8)	96(6)	155(4)•	15(10)	152(9)	0	120(4)•	40	4	91	6	100	25
D. Cupferron (5 gm./liter soln.) + copper	163(9)	107(9)	172(5)•	55(8)	135(9)	0	20(3)•	34	+6	66	17	100	88
E. Cuprammonium	161(9)	90(10)	174(3)•	81(9)	127(9)	42(10)	18(5)•	44	+8	50	21	74	88
Untreated	159(7)	116(6)	0	25(9)	0	0		27	100	84	100	100	100
Necessary difference in av. of 10 breaks for significance at 5% level	17	10	—	16	21	16	—						

• *Total possible, five breaks.* *Note:—Figures in parenthesis represent the number of "good" breaks on which the average has been based, jaw breaks being discarded.*

L = Leached. *W = Weathered.*

TABLE IV

INCREASE IN CUPRAMMONIUM FLUIDITY ON WEATHERING

Treatment	Fluidity (reciprocal poises)		
	Original	Weathered	Increase on weathering
A. Cupferron (25 gm./liter soln.) + copper	2.3	19.7	17.4
B. Cupferron (25 gm./liter soln.) + cuprammonium	3.6	18.5	14.9
C. Cupferron (25 gm./liter soln.) + copper + iron	2.7	26.3	23.6
D. Cupferron (5 gm./liter soln.) + copper	3.1	20.3	17.2
E. Cuprammonium	3.1	19.9	16.8
Untreated	3.4	12.5	9.1

TABLE V

DECREASE IN COPPER CONTENT ON WEATHERING

Treatment	Copper content, %		Copper loss on weathering, % of orig.
	Original	Weathered	
A. Cupferron (25 gm./liter soln.) + copper	0.44	0.06	86.3
B. Cupferron (25 gm./liter soln.) + cuprammonium	0.52	0.08	84.5
C. Cupferron (25 gm./liter soln.) + copper + iron	0.13	0	100
D. Cupferron (5 gm./liter soln.) + copper	0.26	0	100
E. Cuprammonium	0.57	0.08	85.9

Discussion

It will be seen that the application of the various treatments did not affect the breaking strength of the original fabric.

On weathering, the Cupferron–metal treatments applied from 25 gm. per liter solutions of Cupferron (*A*, *B*, and *C*) showed breaking strength losses of approximately 40%, considerably higher than the loss (27%) shown by the untreated sample. All the treated samples showed increases in cuprammonium fluidity which were considerably greater than that of the untreated fabric. These data indicate that the treated samples suffered considerable actinic degradation during exposure and it would seem that the extent of this degradation shown by the Cupferron treated samples was of the same order or greater than that resulting from the straight cuprammonium treatment.

Substantial losses of copper occurred in all cases, there being complete loss of copper from the samples (*C* and *D*) having the lowest copper contents (0.13 and 0.26%).

The resistance of all the treated fabrics to soil burial with preliminary leaching was considerable, that of the Cupferron plus copper–iron being considerable after eight weeks.

Resistance of the weathered samples to soil burial for two weeks was shown by the samples containing the Cupferron–copper treatments (*A*, *B*, and *D*) and by the cuprammonium treated sample (*E*). The resistance of the samples treated with Cupferron–copper–iron and with the lower concentration of Cupferron–copper was considerably reduced by weathering, probably owing to the removal of copper. When compared with the sample treated with cuprammonium alone, it will be noted that the breaking strength losses of the Cupferron–copper treatments applied from a 25 gm. per liter solution of Cupferron (*A* and *B*) are similar but that the Cupferron–copper treatment applied from a 5 gm. per liter Cupferron solution (*D*) produced a somewhat greater loss. The sample treated with Cupferron–copper–iron (*C*) showed a still greater loss.

The increase in cuprammonium fluidity resulting from weathering was highest with the Cupferron–copper–iron treated sample, the increases shown by the other treated samples being of the same order.

The loss of copper on weathering shown by the Cupferron–metal treated samples was similar to or greater than that shown by the cuprammonium treated sample (*E*), the greatest losses occurring with the samples (*C* and *D*) which originally contained the smallest amounts of copper.

It may therefore be concluded that the application to cotton duck of the ammonium salt of nitrosophenylhydroxylamine followed by the precipitation of the copper chelate complex or of the mixed copper–iron chelate compound imparts considerable resistance to rotting as judged by the soil burial test, but that these treatments also cause an increase in the amount of actinic degradation occurring in cotton duck on weathering as compared with that shown by untreated duck, this increase in degradation being of the same order as that produced by a cuprammonium treatment. The chelate copper complex does not show any greater resistance to weathering than does the standard cuprammonium treatment.

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LABORATORY STUDY OF GERMAN BUNA S-3 CHEMICAL RUBBER[1]

By J. W. L. Fordham,[2] A. N. O'Neill,[3] and H. Leverne Williams[4]

Abstract

The German general purpose tire rubber, Buna S-3, differed from the chemical rubber produced in Canada. The study of the polymerization recipe used for this polymer centered around the role of the regulator in the system. The German technique resulted in a system in which the dilute solution viscosity of the polymer remained relatively constant during the reaction. It was found that this system could be duplicated in the laboratory using the equivalents of the German materials. Methods of analysis for diproxid in solution and in latex were investigated. It was observed that the diproxid disappeared very rapidly from the system and the regulating index was found to be similar to that of tertiary amyl mercaptan and to lie between that of *n*-dodecyl and *n*-tetradecyl mercaptan when all were used in the Buna S-3 system. The polymers produced compared favorably with the German polymer as to molecular weight homogeneity, response to heat softening, and other data. Substitution of tertiary amyl mercaptan in the Buna S-3 system resulted in a polymer very similar to that produced using diproxid, and the reaction rate was increased nearly fivefold. The polymer prepared with diproxid and other regulators in this system seemed to be more homogeneous than those prepared by the Mutual formula.

Introduction

Copolymers had been prepared by Hofmann (9) but the true worth of copolymers was revealed in the appearance of Buna S, a copolymer of butadiene and styrene (18, 19, 20, 21).

Buna S possessed reasonably acceptable properties but was exceedingly difficult to process. The practice arose, therefore, of heat softening the polymer before the final compounding (11).

During the shortages of oleates and linoleates the industry had had to use paraffinic fatty acids entirely (0.5 part) and it was found that under those conditions the polymer was much tougher. This toughness could be overcome by adding a regulator, the one which they preferred being diproxid (2, 22, 23, 25) (diisopropylxanthogen disulphide, 0.1 part). The polymer which was produced in quantity by such a system from 1943 on was known as Buna S-3. The copolymer was not only easier to process but the vulcanizates had superior physical properties.

The recipe for Buna S-3 was somewhat similar to the Mutual formula used for GR–S, the wartime Canadian chemical rubber (10, 29, 33, 34). A comparison between the two recipes is given in Table I.

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TABLE I

COMPARISON OF BUNA S-3 AND GR-S RECIPES

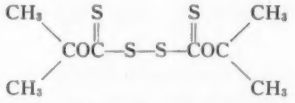
	Buna S-3		GR-S	
Butadiene	70	parts		71.5 parts
Styrene	30	"		28.5 "
Water	105	"		180.0 "
Emulsifier				
Nekal BX (SA-178)	4.5	"	S.F. soap flakes	4.3 "
Paraffinic fatty acid	0.5	"		
Sodium hydroxide	0.3	"		
Regulator				
Diproxid	0.1	"	Dodecyl mercaptan	0.45 "
Initiator				
Potassium persulphate	0.45	"		0.23 "
Shortstop*				
Phenyl-β-naphthylamine	3.0		Hydroquinone	0.15 "
Antioxidant*			BLE	1.5*
Coagulant*				
Calcium chloride	6.0		Sodium chloride	12.0
Acetic acid	0.80		Sulphuric acid	0.9
Ferrous sulphate	0.12			

* *Based on 100 parts of copolymer.*

The ratio of styrene to butadiene was greater in the Buna S-3 system because the diproxid was added in portions as a solution in styrene and consequently some of the styrene had to be withheld from the reaction during the initial stages. The water content was considerably less.

The emulsifier consisted of the Nekal BX, paraffinic fatty acid (C_{12}—C_{15}) and sodium hydroxide. The Nekal BX was about 80% pure; the remaining 20% was sodium sulphate—a desirable impurity which aided in preventing precoagulation during polymerization. The paraffinic fatty acid was added to assist in the processing of the rubber during subsequent compounding. Enough caustic was used to neutralize the fatty acid and to bring the pH of the water up to 11–12. The pH would be high enough throughout the entire reaction to ensure a satisfactory rate.

The regulator



was added in three equal portions in a styrene solution at 0, 20, and 40% conversion. It disappeared much faster than did the dodecyl mercaptan (12) in the GR-S system and hence increment addition was a necessity if a uniform raw polymer viscosity was to be maintained throughout the reaction.

The shortstop (stopping agent) used in the Buna S-3 system was phenyl-β-naphthylamine. This compound was not as effective as hydroquinone, and consequently the residual unreacted monomers had to be removed immediately.

However, the phenyl-β-naphthylamine acted as an antioxidant or stabilizer for the rubber also and was the preferred antioxidant when the rubber was to be heat softened.

The coagulants used in the Buna S-3 system were different from those in the GR–S system. Calcium chloride was used in place of sodium chloride because the Nekal-emulsified latex was more stable than the soap-emulsified latex. Acetic acid was used in place of sulphuric acid because the former was volatile and disappeared during drying of the copolymer, leaving no residual acid to attack the cords and fabrics in the final manufactured product. Acetic acid coagulated polymers also heat softened more readily than did sulphuric acid coagulated polymers. The ferrous sulphate was used to catalyze the thermal breakdown. The coagulants and the latex had to be dilute enough to ensure complete coagulation and yet concentrated enough to ensure a large porous crumb suitable for rapid drying.

The reaction was allowed to proceed at about 45° C. until a conversion of 60% was reached, at which time the reaction was stopped by addition of phenyl-β-naphthylamine and the residual monomers were removed. The reaction required 30 to 36 hr. to reach 60% conversion compared with 12 to 16 hr. at 50° C. required for the GR–S system to reach 72% conversion at which time the GR–S reaction is stopped. The Buna S-3 reaction was not allowed to go beyond 60% conversion because of gel formation. Some gel was formed even at this conversion, but it was very loose (swelling volume > 100) and broke down readily on milling or heat softening.

More regulator was not used to give a lower Mooney rubber and make heat softening unnecessary because increasing the diproxid, while decreasing the Mooney, depreciated the physical properties in comparison with those of the underregulated, heat softened copolymer.

Since many polymers became insoluble on coagulation and handling they used latex extraction to obtain solutions for precise measurements on their polymers.

Techniques

The polymerization reaction was carried out in 4- or 8-oz. bottles fitted with metal screw caps and suitable gaskets (14) to permit hypodermic syringe sampling (16), or in 32-oz. crown cap bottles fitted similarly.

The monomers were pre-emulsified with the emulsifier and water by end over end rotation of the bottles for one hour in a bath maintained at 45° to 50° C. The resulting emulsion had a pH of 12. After pre-emulsification the initiator solution was injected into the bottles by means of a hypodermic syringe. Conversion was followed by hypodermic syringe sampling and determination of per cent solids. The regulator was added in varying amounts and at various conversions as a solution of diproxid in styrene. Bottles were removed periodically throughout the reaction, and aqueous solution of hydroquinone (or styrene solution of phenyl-β-naphthylamine) was added as a shortstop and final conversions were determined.

The following procedures were used to characterize the polymer.

For the vistex viscosity (dilute solution viscosity by complete solution of latex in mixed solvents) a 1 ml. sample of latex was taken by means of a 5 ml. syringe. The sample was released into 50 ml. of a rapidly agitated chlorobenzene–pyridine mixture (75 volume % chlorobenzene, 25 volume % pyridine). The solution was transferred to a 100 ml. volumetric flask and made up to the mark. A clear solution was obtained after the mixture had been allowed to stand 15 min. The samples did not need to stand longer than the time for the above manipulations in order to come to equilibrium. This solution was filtered through glass wool. The concentration was determined by evaporating 20 ml. to dryness and weighing the residue. The weight of residue was corrected for nonrubber solids in those experiments so designated. Viscometric flow times were determined at 30° C. on the original solution and on two dilutions with the above solvent mixture. For a blank or "pure solvent" flow time the above procedure was repeated using a sample from a bottle containing an unreacted Buna S-3 emulsion containing all ingredients with the exception of the potassium persulphate.

For the determination of these "three point" viscosities a modification of the Ubbelohde type viscometer was developed. This modification consisted of replacing the small 15 ml. reservoir bulb of the viscometer with a 100 ml. bulb. This permitted all dilutions to be made in the viscometer and eliminated the necessity of rinsing it after each determination.

The following designations were used:

$$\text{Specific vistex } t_{v_{sp}} = \frac{t \text{ solution}}{t \text{ "blank solvent"}} - 1$$

$$\text{Vistex } [t_v] = \lim_{C \to 0} \frac{t_{v_{sp}}}{C}$$

in which C is in concentration in grams per 100 ml. of solution and t is flow time in seconds. If instead of flow times the kinematic viscosities were used the extrapolation gave the intrinsic vistex viscosity $[\eta_v]$. Later the method was modified by using 80/20 benzene/isopropanol mixture and finally modified again by using the 80/20 benzene/isopropanol mixture but diluting with benzene rather than with the mixture. The latter method gave the true intrinsic viscosity or intrinsic flow time. Direct extraction of the latex with benzene or cyclohexane did not achieve satisfactory results but was sufficiently promising to suggest further development.

To determine the intrinsic flow time and gel content of the dry polymer the remainder of the latex from each bottle, containing 1.5% antioxidant based on the polymer present, was steam distilled at atmospheric pressure to remove the unreacted monomers and the latex coagulated with a calcium chloride – acetic acid – ferrous sulphate mixture. The resulting polymer was washed, and dried at 190° F. for 30 min. From 0.2 to 0.4 gm. of the polymer was weighed accurately and added to about 80 ml. of purified benzene. After standing in the dark for 24 hr. the volume was made up to 100 ml. The

solution was filtered through glass wool and the concentration determined by evaporating 20 ml. to dryness and weighing the residue. Per cent gel (benzene insoluble) was calculated. Flow times were determined for the original solutions and for two dilutions with benzene. The following designations were used:

$$\text{Specific flow time } t_{sp} = \frac{t \text{ solution}}{t \text{ benzene}} - 1$$

$$\text{Intrinsic flow time } [t] = \lim_{C \to 0} \frac{t_{sp}}{C} .$$

If instead of flow times the kinematic viscosity is used then the extrapolation gives intrinsic viscosity $[\eta]$.

Diluting the vistex mixture with benzene also allowed extrapolation to zero nonsolvent, i.e., gave the true intrinsic viscosity, as shown in Table II.

TABLE II

COMPARISON OF VISCOSITY AND VISTEX VISCOSITY RESULTS

Sample No.	Vistex		Dilute solution viscosity in benzene
	Diluting with benzene/ isopropanol mixture	Diluting with benzene alone	
1	2.18	2.85	2.83
2	2.17	2.84	2.88
3	2.20	2.83	2.79
4	2.30	2.96	2.96
5	1.95	2.68	2.54
6	2.25	2.96	2.96

This technique shortened the time for determination of intrinsic viscosity to about one hour and was much more convenient than the usual technique. More detailed studies of vistex (15) and viscosity (4, 32) have been published recently.

The swelling index was the weight of swollen gel divided by the weight of the gel.

An analytical method suitable for the analysis of diisopropyl xanthogen disulphide in latex was highly desirable in order that the rate of disappearance of this compound during the polymerization could be studied. Three methods of analysis for diproxid were tried.

The first method was reduction of diproxid in an alkaline solution with zinc dust and titration of the resulting xanthate with iodine.

Results using this method indicated that the recovery was excellent from pure solutions, varying from 97 to 99%. Recoveries of diproxid from latex varied from 102 to 107%. These recoveries were possible only when the amount of diproxid under analysis was between 10 and 100 mgm., an amount much greater than likely to be met in an analysis of a Buna S-3 latex.

Treatment of diproxid in alcohol solutions with potassium cyanide yields the monosulphide and potassium thiocyanate (3, 31, 41). The latter may be determined either colorimetrically by means of the ferric thiocyanate reaction or by oxidation to the sulphate with excess iodate and back titration of the iodate with thiosulphate.

The Klett-Summerson colorimeter was calibrated with standard potassium thiocyanate solution and with standard solutions of diproxid. For low concentration the results obtained by this method showed an excellent recovery (90 to 100%) and a high degree of reproducibility for amounts greater than 1 mgm.

The third method used the polarograph and was suggested and developed by Kolthoff*.

The arrangement of the polarographic cell is shown in Fig. 1. A Model XII Heyrovsky recording polarograph was used.

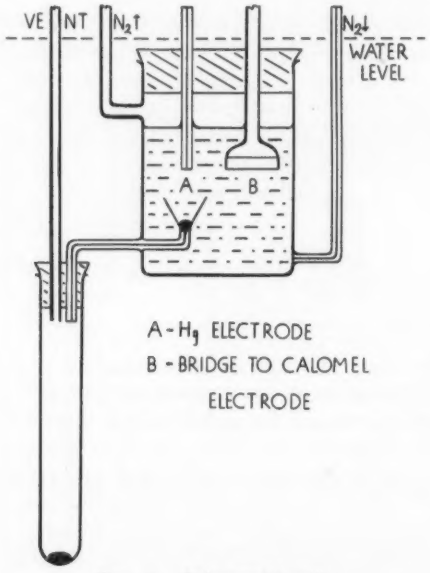


FIG. 1. *Polarograph cell.*

Two samples of diproxid were available, B.F. Goodrich Chemical Company diproxid (recrystallized twice from ethanol, m.p. 57° to 58° C.) and a sample obtained from Germany (recrystallized twice from ethanol, m.p. 57° C.).

Results are shown in Table III. Current readings are in galvanometer scale divisions calculated to the highest sensitivity.

The diffusion current was not directly proportional to the concentration of diproxid, but not sufficiently irregular to render a calibration curve difficult.

* *Private communication through Office of Rubber Reserve.*

TABLE III

POLAROGRAPHIC DATA

Concentration of final solution Molar	Residual current, *IR*	Diffusion current, *ID*		*ID* − *IR*		$\frac{ID - IR}{C}$	
		B.F. Good.	German	B.F. Good.	German	B.F. Good.	German
3.70×10^{-4}	86	465	510	379	424	1.02	1.14
1.85×10^{-4}	86	255	290	169	204	0.91	1.10
0.74×10^{-4}	86	145	160	59	74	0.80	1.00
3.70×10^{-5}	86		124		38		1.03
2.59×10^{-5}	86		112		26		1.01
1.85×10^{-5}	86		110		24		1.30
1.48×10^{-5}	86		104		18		1.22
1.11×10^{-5}	86		101		15		1.36
0.74×10^{-5}	86		95		9		1.21
3.7×10^{-6}	86		90		4		1.08

The results also showed that the German diproxid registered up to 1/4 greater diffusion current for the same weight concentration. This can only be interpreted as due to difference in purity of the two compounds. The following analytical data would also indicate a difference in purity of the two samples of diproxid.

	B. F. Goodrich	I. G. Farben.	Calculated
M.p.	57–58.5° C.	57.0° C.	—
Carbon	36.03	35.74	35.56
Hydrogen	5.77	5.46	5.18

However, the two samples were judged to be essentially identical with respect to regulator action as shown later.

Experimental

Diproxid Disappearance

In order to obtain the rate at which diproxid disappeared during the polymerization, 0.4 or 0.5 part of diproxid, all added initially instead of 0.09 part added in three increments, was used. This larger amount was used since none of the analytical methods were sensitive enough for small amounts. Diproxid analyses obtained using the colorimetric procedure outlined above gave the results shown in Fig. 2.

Curves *A* are the time–conversion curves, the upper obtained at 45° C. and the lower at 50° C. The corresponding residual diproxid disappearance curves (*B*) indicate that the rate of disappearance is quite rapid. Only a very small amount remains after 20 to 25% conversion. There is some suggestion that the rate of disappearance is increased by increased temperature (lower curve). If the rate of disappearance is first order these results would be applicable at lower concentrations of diproxid as well.

Comparison of German and American Regulators

Tables IV and V show the polymerization data obtained at 50° C. and at 45° C. Table V also shows a comparison of the I. G. Farbenindustrie and B. F. Goodrich Chemical Company samples of diproxid. No vistex viscosity

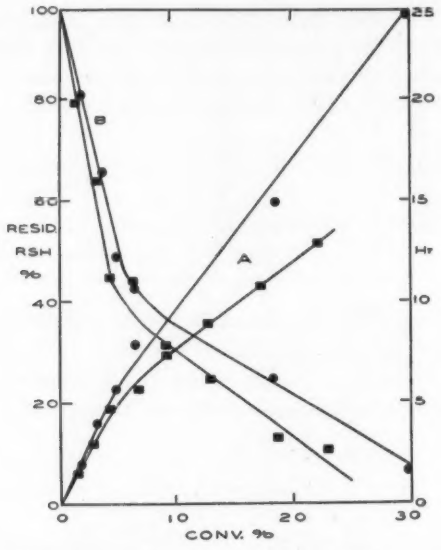


FIG. 2. *Diproxid disappearance in the Buna S-3 system; (A) time–conversion, (B) residual diproxid–conversion.* ● *8 oz. bottle, 3.10 parts Nekal, 1.4 parts* Na_2SO_4, *45° C.* ■ *32-oz. bottle, 4.00 parts Nekal, 0.7 parts* Na_2SO_4, *50° C.*

TABLE IV

BUNA S-3 POLYMERIZATION AT 50° C.

(0.09 part of diproxid added in increments of 0.03 part at 13, 30, and 45% conversion)

Time, hr.	Conversion, %	$[t_s]$	$[t]$	Gel, %
5.5	13.2	2.30	4.75	14.4
10.5	25.2	2.30	4.10	25.8
15.75	37.2	2.30	3.60	26.1
22.75	51.0	1.90	2.50	26.4
30.0	65.0	1.30	1.50	55.5

data were determined on this series (Table V) but Table VI shows the vistex results obtained on an identical group. It is evident that the regulating activities are essentially identical. The results are much more consistent when the vistex viscosity is used rather than the dilute solution viscosity. In general, too, the rate of conversion is slow and the viscosity decreases with increasing conversion as the gel increases.

TABLE V

POLYMERIZATION AT 45° C.

(0.09 part of diproxid added in increments of 0.03 part at 13, 30, and 45% conversion)

Time, hr.	Conversion		[η]		Gel	
	German diproxid	Goodrich diproxid	German diproxid	Goodrich diproxid	German diproxid	Goodrich diproxid
5	7.2%	7.2%	4.70	4.25	5.5%	6.0%
13	19.5	20.3	4.85	5.50	17.5	8.0
20	30.6	30.3	3.00	4.70	61.5	11.0
29	41.7	43.7	3.15	2.25	23.0	49.5
34	49.8	49.8	3.80	2.95	9.5	4.0
41	59.2	59.2	2.50	2.70	5.0	35.5

TABLE VI

POLYMERIZATION AT 45° C.

(0.09 part of diproxid added in increments of 0.03 part at 13, 30, and 45% conversion)

Time, hr.	Conversion		$[\eta_v]$	
	German diproxid	Goodrich diproxid	German diproxid	Goodrich diproxid
8.5	13.6%	13.6%	3.90	3.90
13.0	21.0	22.0	3.20	3.30
20.0	29.0	29.0	2.90	2.95
26.5	39.0	39.5	2.55	2.60
34.0	48.0	51.0	2.20	2.20
41.75	58.0	58.0	1.90	2.10

Polymerization Data

Figs. 3 and 4 and Tables VII and VIII record the polymerization data obtained in investigating the possibility of observing a constant vistex value throughout the reaction. These data were obtained by varying the time and amounts of regulator increments. Fig. 3 gives the data for an unregulated system. Curve *A* is the time–conversion curve and Curve *B* the viscosity–conversion curve. The latter can be seen to reach a peak at about 10% conversion. The former is S-shaped. Fig. 4 gives the data for a system in which various amounts of diproxid were added at 13% conversion, and 0.06% diproxid at 8% conversion; before the peak of the vistex–conversion curve was reached. An additional 0.03% was added at 33% conversion. Of the lower pair, Curve *A* is the time–conversion curve for the first series and Curve *B* for the second experiment. Of the upper pair, Curve *A* is the viscosity–conversion curve for the first series and divides into three branches. Branch 1 resulted from 0.015% diproxid at 13% conversion, branch 2 from 0.030% similarly, and branch 3 from 0.060%. On the other hand, the addition of 0.06% at 8% conversion and 0.03% at 33% conversion resulted

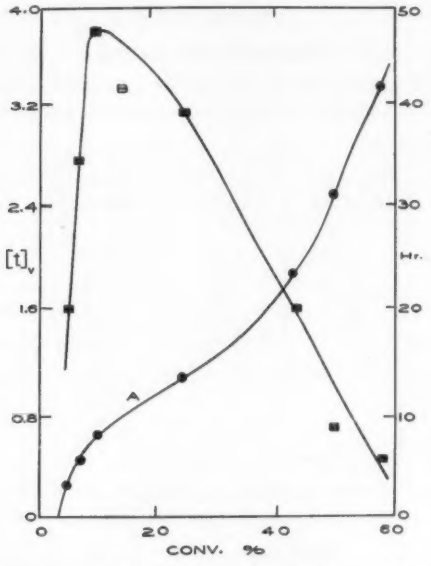


FIG. 3. *Polymerization carried to 60% conversion with no regulator present; (A) time–conversion, (B) viscosity–conversion.*

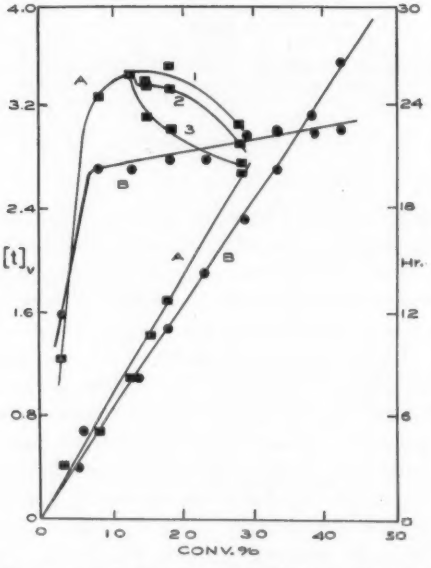


FIG. 4. *Effect of time and amount of diproxid addition. Curves (A) diproxid added at 13% conversion; branch (1) 0.015%; branch (2) 0.030%; branch (3) 0.060%. Curves (B) 0.060% at 8% conversion and 0.030% at 33% conversion. Lower curves, time–conversion; upper, viscosity–conversion.*

in Curve *B*, which is considered reasonably constant although lower than desirable. It can be seen that the viscosity remains quite constant to 42.5% conversion in the latter case.

The latex of the polymers of 38 and 42.5% conversion (Fig. 4, Curve *B*) were divided into two samples each. One-half of each was coagulated with isopropanol and dried *in vacuo* for two hours. The remaining portions of each were coagulated with calcium chloride and acetic acid. Antioxidant was added before coagulation (1.5% BLE based on polymer by weight). The polymers were dried in a hot air oven at 190° F. for 30 min. All polymers showed 100% solubility in benzene. The polymers obtained by coagulation with isopropanol exhibited identical $[\iota]$ values of 4.00 while those coagulated with calcium chloride and acetic acid possessed a lower value of 3.50. These data indicate the high molecular weight of the polymer and the effect of the type of coagulation on the molecular weight of the resultant dry polymer.

In the next three series each sample was an individual 8-oz. charge. The data are collected in Table VII. From these it can be seen that rate of reaction at 45° C. is about 2% conversion per hour. The vistex viscosity using benzene/isopropanol solvent is somewhat lower than the dilute solution viscosity of the same sample, and the vistex viscosity in chlorobenzene/pyridine solvent approximates the dilute solution viscosity. The dilute solution viscosity–conversion curves are not as horizontal as desired. The gel content of the coagulated sample was not consistent but was low usually.

The polymers for viscosity studies coagulated by the special alcohol technique were treated under as nearly as possible air-free conditions. The stopped but unstabilized latex was released into ethanol through which nitrogen had been bubbled, and the syringe weighed before and after in order to obtain the exact weight of polymer transferred. The nitrogen was bubbled through until the rubber had been thoroughly washed, the ethanol was drained off, the tube closed with a glass stopper and the sample dried by evacuation of the chamber at room temperature. As soon as the sample was dry it was removed from the screen and added directly to benzene. A check on the subsequent concentration of rubber in the benzene solution indicated no appreciable loss of material.

When the polymerization was carried out in 32-oz. bottles the samples represented small amounts withdrawn by syringe. The data are in Table VIII. Most of the final samples were stabilized with three parts of phenyl-β-naphthylamine added as an emulsion or in styrene solution, and were coagulated with calcium chloride – acetic acid – ferrous sulphate coagulant, and the Mooney was determined. Half of the sample was then heat softened in a Dietert Moisture Tester at 140° C. for 90 min. and the Mooney determined again as was also the gel, dilute solution viscosity, and swelling index. These results are in Table IX and include similar data for a sample of German Buna S-3. The calculated intrinsic viscosities were based upon the work of Back (1) from which the results for natural rubber are quoted.

TABLE VII

POLYMERIZATION DATA

Sample No.	Time, hr.	Conv., %	Vistex		[η]	Gel, %	Comment
			Chloro/ pyridine	Benzene/ isoprop.			
A. Diproxid: 0.06 at 6% conv., 0.03 at 45.5% conv., 45° C.							
0	0.0	0.0	0.00	0.00	0.00	0.0	Hydroquinone (HQ 0.17/100 mon.
1	4.0	4.7	5.35	3.85	4.35	0.0	BLE 1.5/100 rubber
2	8.0	14.2	3.25	2.95	3.00	0.0	
3	12.1	25.2	3.00	2.75	3.10	0.0	1–3 Brine-acid coag.
4	16.0	34.1	4.00	3.40	3.60	2.0	4-8 $CaCl_2$–HOAc coag.
5	19.9	42.9	4.05	3.60	4.40	7.0	
6	24.0	50.2	—	3.40	3.05	30.0	
7	28.0	59.7	2.65	2.60	2.40	42.0	
8	33.5	68.3	2.20	2.35	1.55	65.5	
B. Diproxid: 0.06 at 10.8% conv., 0.03 at 38.9% conv., 45° C.							
0	0.0	0.0		0.00	0.00	0.0	HQ 0.17/100 mon.
1	3.0	5.3		6.00	3.60	0.0	BLE 1.5/100 rubber
2	6.0	12.2		3.95	3.60	2.5	
3	9.5	20.4		4.30	4.75	9.0	1–6 $CaCl_2$–HOAc coag.
4	12.0	24.6		3.55	4.30	10.0	
5	15.0	33.6		3.70	4.40	8.0	
6	18.0	40.2		3.60	4.40	7.5	7–8 Isopropanol coag.
7	21.0	49.0		3.55	4.30	2.0	
8	24.0	56.7		3.10	3.05	57.5	
C. Diproxid: 0.03 at 0.0, 12.8, and 24.4% conv., 45° C.							
0	0.0	0.0		0.00	0.00	0.0	HQ 0.17/100 mon.
1	3.0	3.0		2.00	1.50	0.0	Coag. and dried by special technique and placed directly in benzene
2	6.0	7.3		3.65	2.15	0.0	
3	9.0	11.3		2.50	2.35	0.0	
4	12.0	13.4		2.60	2.15	0.0	
5	15.0	9.3		3.25	2.10	0.0	
6	18.0	24.1		2.60	2.60	0.0	
7	21.0	28.8		2.45	2.65	0.0	
8	24.0	40.0		2.90	3.15	0.0	

It can be seen that as the experiments proceed (Table VIII) the viscosity–conversion curves become quite horizontal. In some cases there is considerable gel but this is very loose. In one sample the gel dropped from 90% to 30% upon massing the sample for Mooney determination. The ratio of $[\eta]/[\eta_v]$ is about 1.3.

The ratio of the heat softened Mooney to the original Mooney is noted to be quite constant for high Mooney polymers in proportion. The high Mooney

TABLE VIII

POLYMERIZATION DATA

Sample No.	Time, hr.	Conv. %	$[t_v]$	$[t]$	Gel, %	Swelling index	$[t]/[t_v]$
A. Diproxid: 0.03 at 2.7 and 14.8% conv., 0.06 at 24.3% conv., 50° C.							
0	0.0	0.0	0.00	0.00	0.0		—
1	2.0	2.7	1.75	4.20	85.5		2.40
2	4.0	5.4	2.05	3.05	55.0		1.49
3	6.0	9.0	2.00	3.10	30.0		1.55
4	8.5	14.8	1.95	3.10	18.0		1.59
5	10.0	16.5	2.05	3.05	12.0		1.49
6	12.0	21.8	2.00	2.65	12.0		1.32
7	13.0	24.3	2.05	2.55	16.5		1.24
8	23.5	41.4	1.25	2.05	10.0		1.64

(NOTE: *Intrinsic flow time not corrected for nonpolymer solids to this point, all values corrected hereafter, also intrinsic viscosity and intrinsic vistex viscosity used hereafter.*)

			$[\eta_v]$	$[\eta]$			$[\eta]/[\eta_v]$
B. Diproxid: none, 50° C.							
1	2.5	3.7	6.50	8.90	38.5		1.37
2	4.5	6.6	8.85	9.05	45.5		1.02
3	6.5	12.7	7.20	9.95	12.0		1.38
4	8.0	17.1	6.65	6.30	74.5		0.95
5	9.5	19.0	6.35	6.40	63.5		1.01
6	11.0	21.7	5.50	6.15	69.0		1.12
7	12.5	27.0	5.00	6.60	20.5		1.32
8	24.0	53.7	1.85	5.15	89.0		2.79
C. Diproxid: 0.03 at 0.0, 18.5, and 35% conv., 45° C.							
1	6.5	8.2	3.75	5.15	11.0	98.0	1.38
2	8.5	11.4	3.35	4.50	8.0	43.0	1.34
3	10.5	15.3	3.45	4.35	2.5	39.0	1.26
4	12.5	18.3	3.65	4.65	1.0	145.0	1.27
5	30.5	40.8	3.95	6.30	19.5	62.0	1.59
6	32.5	43.2	4.10	5.25	29.5	118.0	1.28
7	35.5	48.2	4.20	3.70	84.5	54.0	0.88
8	41.0	53.5	3.05	4.05	79.5	51.5	1.32
D. Diproxid: 0.04 at 0, 18.0, and 30.5% conv., 45° C.							
1	9.0	14.2	2.90	3.95	0.0		1.36
2	12.5	22.5	2.85	3.70	0.0		1.30
3	16.0	27.7	2.80	3.40	0.0		1.21
7	21.5	30.5	2.80	3.40	0.0		1.21
8	27.5	39.3	2.75	3.25	0.0		1.18
4	33.0	50.4	2.90	3.65	0.0		1.26
5	36.0	54.3	2.95	3.90	0.0		1.13
6	39.5	57.2	3.25	3.75	41.0	85.0	1.15

TABLE VIII—*Concluded*

POLYMERIZATION DATA—*Concluded*

Sample No.	Time, hr.	Conv. %	$[\eta_s]$	$[\eta]$	Gel, %	Swelling index	$[\eta]/[\eta_s]$
E. Diproxid: 0.05 at 0, 14.8, and 28.6% conv., 45° C.							
1	9.2	13.4	2.50	3.25	0.0		1.30
2	12.3	18.3	2.50	3.70	0.0		1.47
3	15.8	23.9	2.50	3.15	0.0		1.26
7	26.0	28.6	2.45	2.60	0.0		1.06
8	29.6	32.8	2.15	2.30	0.0		1.07
4	33.2	46.8	2.75	3.55	0.0		1.29
5	36.4	50.7	3.05	3.90	0.0		1.28
6	40.3	54.9	3.30	4.25	0.0		1.29
F. Diproxid: 0 .06 at 0, 23.8, and 42.4% conv., 45° C., 4.0 parts Nekal, no Na_2SO_4							
1	10.2	14.9	2.28	2.88	0.0		1.26
2	13.4	23.8	2.40	3.07	0.0		1.28
3	16.8	29.9	2.39	2.97	0.0		1.24
4	34.2	67.5	3.49	4.77	70.0	21.0	1.36
5	36.2	71.1	2.93	3.81	89.5	30.5	1.30
6	37.2	73.4	2.69	3.50	91.0	51.5	1.30
G. Diproxid: 0.06 at 0.0, 19.3, and 43.9% conv., 50° C., 4.0 parts Nekal, no Na_2SO_4							
1	6.2	13.0	1.90	2.45	0.0		1.29
2	8.4	19.3	2.29	2.94	0.0		1.28
3	12.0	30.2	2.29	2.92	0.0		1.27
4	15.0	43.9	2.29	2.98	0.0		1.30
5	17.4	50.7	2.58	3.47	0.0		1.35
6	19.6	58.7	2.80	3.65	1.0	4.80	1.30
H. Diproxid: 0.07 at 0, 23.4, and 38.7% conv., 50° C., 4.0 parts Nekal, no Na_2SO_4							
1	6.2	21.4	2.72	3.18	33.5	107.0	1.17
2	7.0	23.4	2.85	3.75	27.5	81.0	1.32
3	9.0	28.0	2.58	3.54	2.5	200	1.37
4	12.6	38.7	2.42	3.05	0.0		1.26
5	16.6	47.0	2.20	2.99	0.0		1.36
6	20.0	52.2	2.20	2.74	0.0		1.25
I. Diproxid: 0.07 at 0, 22.8, and 40.3% conv., 50° C., 4.0 parts Nekal, no Na_2SO_4							
1	6.2	19.6	2.18	2.83	0.0		1.30
2	8.4	26.1	2.17	2.88	0.0		1.33
3	10.8	33.8	2.20	2.79	0.0		1.27
4	12.8	40.3	2.30	2.96	0.0		1.29
5	15.4	46.5	1.95	2.54	0.0		1.30
6	20.0	58.8	2.25	2.96	0.0		1.32

(*All polymers coagulated as indicated in Table VII, Part C*)

TABLE IX

HEAT SOFTENING OF POLYMERS

Sample No. (Table VIII)	Conv., %	$ML/4'$	$\frac{ML/4'\text{HS}}{ML/4'\text{orig.}}$	Gel, %	Swelling index	$[\eta]_{obs.}$	$[\eta]_{calc.}$*	$\frac{[\eta]_{obs.}}{[\eta]_{calc.}}$
VIII-B-original	53.7	155.5	0.460	31.5	93.5	2.85	4.38	0.650
Heat soft.	—	71.5	—	0.0	—	2.02	—	—
VIII-C-original	53.5	168.5	0.425	62.5	73.0	3.37	4.67	0.722
Heat soft.	—	71.5	—	10.5	134.5	2.17	2.54	0.854
VIII-D-original	57.2	121.5	0.415	0.0	—	3.45	—	—
Heat soft.	—	50.5	—	2.0	360	2.01	2.08	0.967
Original	39.3	95.5	—	0.0	—	4.03	—	—
VIII-E-original	54.9	120.0	0.415	0.0	—	3.51	—	—
Heat soft.	—	49.5	—	0.0	—	2.15	—	—
VIII-F-1 original	37.8	136.5	—	0.0	—	4.16	—	—
F-2 heat soft.	73.4	71.5	—	32.0	70.0	1.56	2.54	0.613
VIII-G-original	58.7	99.0	0.651	0.0	—	3.14	—	—
Heat soft.	—	64.5	—	1.5	570	1.99	2.38	0.837
VIII-H-original	52.2	64.5	0.783	0.0	—	2.38	—	—
Heat soft.	—	50.5	—	0.0	—	2.10	—	—
VIII-I-original	58.8	90.5	0.675	0.0	—	2.56	—	—
Heat soft.	—	61.0	—	0.0	—	2.29	—	—
Natural rubber	—	100.0	—	35.5	—	5.35	1.85	2.90
I. G. Farben Buna S-3								
Original	—	149.5	0.415	4.5	—	3.35	4.24	0.790
Heat soft.	—	62.0	—	4.0	—	2.20	2.33	0.946

* $[\eta]_{calc.} = 0.0219\ ML/4' + 0.97$; $[\eta]$ *that would be obtained if the polymer were gel free.*

copolymers heat softened at a rate comparable to that of I. G. Farbenindustrie Buna S-3. The ratio of $[\eta]_{obs.}/[\eta]_{calc.}$ did not differ much from that for GR–S, nor approach that of natural rubber.

While a horizontal intrinsic viscosity – conversion curve was obtained in the 32-oz. bottle polymerizations by adding 0.070 part of diproxid at 0, and approximately 20, and 40% conversion the intrinsic viscosity and the Mooney plasticity were both lower than those of I. G. Farbenindustrie Buna S-3. The copolymer produced using 0.180 part of diproxid had an intrinsic viscosity increasing at the end of the reaction; no combination using 0.100 parts of diproxid would give the desired gel-free polymer with a horizontal intrinsic viscosity – conversion curve. It is probably very difficult, if not impossible, to duplicate exactly a copolymer manufactured on a plant scale in bottle reactors; the agitation conditions are different.

Regulating Index of Diproxid and Mercaptans

Since the significant difference between Buna S-3 and GR–S lies in the regulator and its mode of addition, it was of prime importance to compare

its effectiveness as a regulator with that of normal and tertiary mercaptans. This was done by measuring (26) the residual mercaptan at various conversions. The data are collected in Fig. 5 and should be compared with the data in Fig. 2.

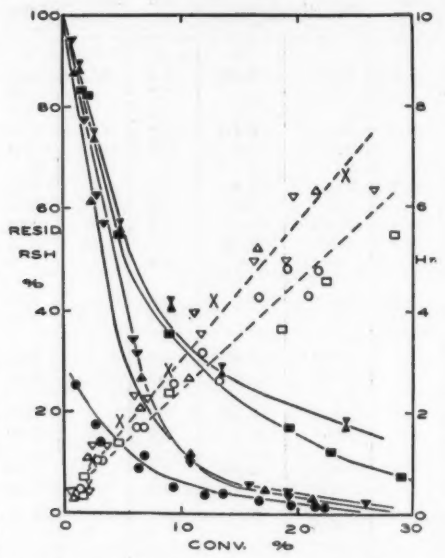


FIG. 5. *Residual mercaptan in Buna S-3 system. Open points, time–conversion; broken lines, representative curve; upper, for normal mercaptans, lower, for tertiary mercaptans. Solid points, residual mercaptan–conversion.* ● *Tertiary butyl 0.2,* ■ *tertiary amyl 0.2,* ▲ *n-decyl, 0.4,* ▼ *n-dodecyl, 0.4,* ⧗ *n-tetradecyl 0.4.*

The time–conversion curves, broken lines, indicate somewhat greater rates of reactions with tertiary mercaptans (lower curve) than with normal mercaptans (upper curve). The solid curves, residual mercaptan – conversion curves, would appear in all cases, except with tertiary butyl mercaptan, to be similar to that for diproxid.

However the activity of the mercaptan is better expressed as regulating index, defined as

$$r = \frac{d \ln R}{dP},$$

in which R is the per cent residual regulator at fractional conversion P, and was found by plotting ln R against P. Extrapolating the initial straight line portion of the resulting graph to zero conversion gave the waste factor defined as the difference between 100 and the intercept. The data are summarized in Table X, including previously published results obtained using the GR–S system (5, 30). The waste factor arises, presumably, from disappearance of mercaptan in side reactions such as disulphide formation.

It is evident that tertiary amyl mercaptan approximates diproxid in its regulating characteristics and that diproxid lies between normal dodecyl and

TABLE X

REGULATING INDEX AND WASTE FACTOR FOR DIPROXID AND MERCAPTANS

Regulator	Regulating index	Waste factor	Reference
In Buna S-3 system			
Diproxid	14.7	0	
tert. butyl mercaptan	16.1, 15.1	0.76, 0.70	
tert. amyl mercaptan	12.9, 12.9	0.0, 0.0	
n-decyl mercaptan	20.0	0.0	
n-dodecyl mercaptan	20.0, 20.0	0.0, 0.0	
n-tetradecyl mercaptan	11.9	0.0	
By Mutual formula			
n-octyl mercaptan	11.0	0.73	5
n-decyl mercaptan	8.5	0.51	5
n-dodecyl mercaptan	2.50	0.0	5
tert. butyl mercaptan	2.35	0.10	5
tert. decyl mercaptan	3.85, 13.7	0.0, 0.64	5, 26
tert. octyl mercaptan	2.80, 3.95	0.0, 0.33	5, 26
tert. dodecyl mercaptan	3.16	0.045	26
tert. hexadecyl mercaptan	0.58	0.0	26

normal tetradecyl mercaptan in its regulating characteristics. Particularly noticeable is the difference in the regulating index for the same mercaptans in the Buna S-3 and GR–S systems. The index is much lower in the latter case.

Use of Mercaptans in Buna S-3 Formula

Polymerization data using tertiary butyl mercaptan are given in Fig. 6 and using tertiary amyl mercaptan, in Fig. 7. These results are quite comparable to those obtained using diproxid. Data obtained when normal mercaptans are used are given in Table XI. Curves *A* of Fig. 6 show the time–conversion curves. The upper of pair *B* indicates the decline in viscosity after 14% conversion, regardless of the amount of mercaptan added. On the other hand, Curve *B* shows a rising viscosity when 0.06% tertiary butyl mercaptan was added at 8% conversion. The ideal must be somewhere between the two values. Better results were obtained with tertiary amyl mercaptan, Fig. 7. Table XI indicates the unsatisfactory use of *n*-octyl mercaptan but encouraging use of *n*-decyl mercaptan.

Heterogeneity of the Molecular Weights

An approximation to the molecular weight distribution may be determined from the viscosity average molecular weight (M_v) and the number average

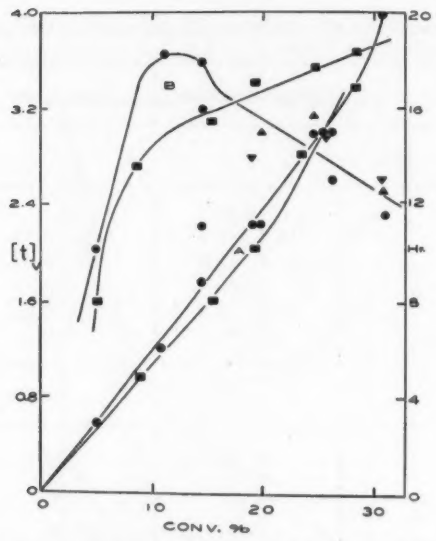


FIG. 6. *Tertiary butyl mercaptan in the Buna S-3 system; (A) time–conversion curves, (B) viscosity–conversion curves.* ● *Mercaptan added at 14% conversion,* ● *0.015%,* ▲ *0.030%,* ▼ *0.060%;* ■ *0.060% added at 8% conversion.*

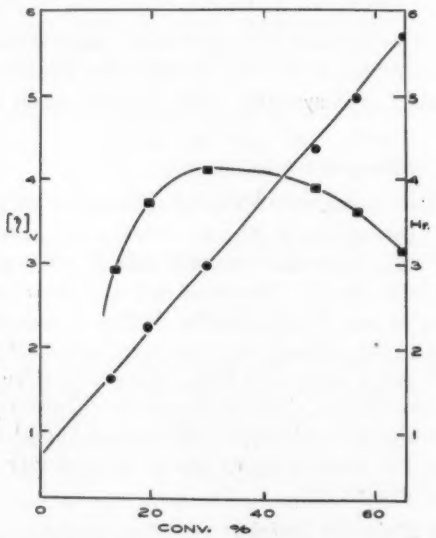


FIG. 7. *Polymerization data using 0.009 parts t-amyl mercaptan at 0, 19, and 49% conversion.* ● *Time–conversion,* ■ *viscosity–conversion.*

TABLE XI

POLYMERIZATION DATA USING NORMAL MERCAPTANS

Time, hr.	Conversion, %	Intrinsic viscosity	Residual mercaptan
n-Octyl mercaptan. 0.06 part at 0, 31, and 47% conv.			
5.2	25.4	4.65	66.9%
6.4	30.9	5.20	66.7
7.6	38.8	4.59	36.7
8.6	47.1	4.00	34.0
10.0	57.5	3.54	1.4
n-Octyl mercaptan. 0.097 part at 0, 19, and 41% conv.			
2.0	6.8	0.55	68.2
4.2	18.6	1.59	66.9
6.2	31.4	1.57	33.9
7.6	40.8	2.22	33.1
9.4	55.1	2.22	0
10.2	62.3	2.74	0
	Final Mooney 46 *ML/4'*		
n-Decyl mercaptan. 0.05 part at 0, 22, and 41% conv.			
2.4	11.2	7.51	67.2
4.2	21.6	3.30	67.2
5.6	30.6	2.90	38.4
7.0	41.4	3.68	38.4
8.0	48.7	3.67	37.7
9.3	57.9	3.68	1.0
	Final Mooney 93.0 *ML/4'*		

by the logarithmic number distribution (Maxwellian type with unlimited range toward infinite molecular weight).

$$dn = \frac{Ne^{-y^2}dy}{\sqrt{\pi}}$$

where $y = \frac{1}{\beta} \ln \frac{M_w}{M_0}$;

dn = number of molecules in the interval y to $y + dy$;

N = total number of molecules;

β = degree of heterogeneity, and is zero for a homogeneous polymer;

M_0 = molecular weight at which the peak occurs in the distribution curve.

From the above relations it may be derived for butadiene/styrene copolymers that:

$$\beta = 2.35 \log R, \text{ where } R = \frac{\overline{M}_w}{\overline{M}_n}, \text{ and } M_0 = \overline{M}_w \cdot R^{-0.598}$$

$\overline{M}_v$ may be determined from the intrinsic viscosity determination and $\overline{M}_n$ from the regulator disappearance curve, assuming that one molecule of regulator is used up per copolymer molecule formed. Assuming that a Buna S-3 sample of 60% conversion with intrinsic viscosity of 3.00 is produced in plant reactors by adding 0.03 part of diproxid at 0, 20, and 40% conversion, the values of β and M_0 will be 1.41 and 11.7×10^4 respectively. Other representative data are in Table XII. The polymers produced in the Buna S-3 system with diproxid would seem to be of more uniform and of higher molecular weight than those produced in the same recipe with normal mercaptans or those produced in the GR–S system.

TABLE XII

HETEROGENEITY OF MOLECULAR WEIGHTS

Polymer	Conv., %	$\overline{M}_v$	$\overline{M}_n$	R	β	$\overline{M}_0$
Diproxid 0.06 at 0 and 0.04 at 40% conversion	10	22.1×10^4	6.06×10^4	3.35	1.70	3.20×10^4
	20	41.5	10.60	3.90	1.81	4.69
	30	68.1	14.40	4.75	1.93	5.68
	40	97.7	18.38	5.30	2.00	6.73
Diproxid 0.06 at 0 and 19 and 0.03 at 38% conversion	10	27.6	6.60	4.20	1.85	2.80
	20	40.4	9.65	4.20	1.85	4.09
	30	40.4	8.25	4.90	1.95	3.18
	40	40.4	9.15	4.40	1.89	3.77
	50	40.6	9.75	4.15	1.85	4.14
	60	64.8	11.15	5.80	2.06	3.80
n-Octyl mercaptan 0.06 at 0, 31, and 47% conversion	20	70.0	5.10	13.70	2.50	10.60
	30	97.7	7.75	13.30	2.49	15.60
n-Octyl mercaptan 0.097 at 0, 19, and 41% conversion	10	6.6	1.55	4.25	1.86	0.66
	20	16.7	1.90	8.70	2.28	0.53
	30	16.7	2.30	7.20	2.17	0.7
	40	26.5	3.05	8.70	2.28	0.63
	50	28.1	2.60	10.90	2.36	0.64
	60	34.0	3.05	11.20	2.36	0.76
n-Decyl mercaptan 0.05 at 0, 22, and 41% conversion	10	13.2	3.60	3.70	1.77	1.64
	20	36.7	7.10	5.15	1.98	2.66
	30	41.5	5.75	7.20	2.18	1.77
	40	54.6	7.05	7.75	2.22	2.07
	50	59.4	6.15	9.65	2.34	1.58
	60	54.4	7.05	8.45	2.26	1.96
n-Dodecyl mercaptan in Mutual formula, 0.5 at 0 conv.	20	3.6	1.8	—	1.30	1.19
	38	9.3	2.4	—	1.81	1.05
	59	15.4	3.1	—	1.97	1.22
	82	32.2	4.0	—	2.24	1.14
Buna S-3, 0.06 diproxid at 0, 20, and 40% conv., constant $[\eta] = 3.00$	60	43.7	9.60	4.55	1.91	2.51

Discussion

It is seen that diproxid is a reactive regulator. At 30% conversion only 6% of the initial amount remained. In regard to our present theories of modification (6, 7, 8, 12, 13, 27, 28, 30, 37, 38, 39, 40) in the emulsion polymerization system this would indicate that increment addition of such a regulator is a necessity if a constant viscosity is to be obtained throughout the reaction.

The rate of polymerization was found to be very sensitive to changes in temperature. A reduction in temperature from 50° C. to 45° C. resulted in a rate decrease from about 2.4% per hour at the higher temperature to about 1.5% per hour at the lower. The significant feature is that this reaction proceeds at a steady rate in the complete absence of a promoter or chain transfer agent. Diproxid is not a promoter, and may indeed be a retarder, particularly in the presence of impurities.

The Buna S-3 polymerization system, although fairly reproducible with regard to conversion is nonreproducible when considering such properties as intrinsic flow time and gel content. However, it is very difficult to see why such anomalies should occur in the polymerization reaction. It is believed that such irreproducible properties might result during the handling of the polymer, i.e., during removal of excess monomers, coagulation of the latex, and drying of the polymer.

Because of the irreproducibility of intrinsic flow time and percentage gel measurements, these methods of characterization were discontinued early in favor of the vistex technique, by which the polymerization reaction may be studied and the "whole" polymer, including soluble and gelled portions, evaluated without the changes brought about during removal of the residual monomers, coagulation of the latex, and drying. By this technique the latex particle is individually dispersed in a mixed solvent system. This results in complete solution or dispersion of both soluble polymer and gel. From the theories of viscosity it is evident that the formation of gel during polymerization will result in an over-all decrease in intrinsic viscosity when the whole-polymer is considered. The complicating feature is that low vistex values may also be obtained with low molecular weight "linear" polymers. Hence, with present methods it is very difficult, in an examination of a vistex–conversion curve, to determine how much of the decrease can be attributed to gel formation and how much to regulation.

From an examination of the data in Fig. 3, which represents the polymerization reaction free from the complications of modification, it is seen that there is a rapid rise in the vistex viscosity from 0 to 13% conversion. This is probably indicative of the formation of polymer molecules of increasing molecule weight and comparatively linear in nature. At about 13% conversion, gel formation begins, owing to branching, cross linking, and increasing molecular weight of the polymer. This results in a continuous falling-off of the vistex to a very low value at the completion of the reaction. Fig. 4 (Curve *A*) shows the same trends except that the formation of gel and consequently

the decrease in vistex is made less pronounced by the addition of regulator after the vistex has reached a maximum value. Fig. 4, Curve *B*, shows a different trend. The results indicate a polymerization in which a constant and fairly high vistex value with increasing conversion was obtained. As was predicted, the polymer produced in this case was entirely free of microgel, as evidenced by the nonexistence of macrogel in the coagulated and dried polymer.

The more comprehensive data in Tables VII and VIII indicate that when corrections are applied for nonrubber constituents it is not easy to obtain a satisfactorily flat vistex viscosity – conversion curve with the smaller amounts of regulator. Indeed best results are obtained with amounts of diproxid of the order of 0.2 part total. The same general trends may be noted with higher diproxid charges as are noted in the preparation of GR–S. The peak of the intrinsic viscosity – conversion curve shifts to higher conversions and the entire curve towards lower viscosities. Increasing the Nekal BX charge increases the rate somewhat and decreases the amount of precoagulum slightly.

The ratio of intrinsic viscosity to intrinsic vistex viscosity varies with the intrinsic vistex viscosity somewhat but was generally rather constant for gel-free samples and could be represented by the equation:

$$[\eta] = 0.175\,[\eta_v]^2 + 0.92\,[\eta_v]$$

Comparative data taken from smoothed-out viscosity conversion and vistex conversion curves are given in Table XIII. Also it was found, following the

TABLE XIII

RATIO OF INTRINSIC VISCOSITY TO VISTEX VISCOSITY

Sample No.	$[\eta]$	$[\eta_v]$	$[\eta]/[\eta_v]$
1	2.45	1.90	1.29
2	2.95	2.30	1.28
3	2.95	2.30	1.28
4	2.95	2.30	1.28
5	3.24	2.54	1.28
6	3.48	2.74	1.27
7	3.42	2.54	1.37
8	3.07	2.30	1.33
9	2.84	2.18	1.30
10	2.85	2.19	1.30
11	2.85	2.20	1.30
12	2.85	2.20	1.30
13	2.87	2.19	1.30

work of Back (1), that $[\eta] = 0.0219 \times ML/4' + 0.97$ for gel-free copolymers, and $[\eta] = (0.0219ML/4' + 0.97) \times (0.93 - 0.0093\ \text{gel})$ for gel-containing polymers. The intrinsic viscosity and the gel were determined on the sample after they were massed for the Mooney determination. This equation differs but slightly from that found by Back for GR–S and is subject to the same limitations.

The regulating indices of mercaptans would seem to be higher in the Buna S-3 system than in the Mutual formula. Of the commonly available materials only tertiary amyl mercaptan would seem to fulfill the conditions of having the same regulating index and the absence of waste factor. Polymer prepared using tertiary amyl mercaptan in amounts corresponding mole for mole to the diproxid should yield the same polymer. This would appear to be true within the ability of the system to discriminate.

However, should the schedule of additions of mercaptan be altered, some other mercaptan would accomplish the same results, the essential requirements being that the activity of the regulator oscillate between two values, both of which are above that which will allow gel formation readily and below that which will result in low molecular weight polymer. These values could be calculated from the data presented in a specific case. It is evident, too, why the use of *n*-dodecyl mercaptan in place of diproxid would lead to the formation of a more heterogeneous polymer when the same schedule of addition was adhered to; the dodecyl mercaptan should be added in smaller molar quantities and more often. The main advantage in replacing diproxid by a mercaptan is the very considerable increase in the rate of the reaction, and the system seems to be more reproducible. The effect of the mercaptans on rate may be arranged in the order tertiary amyl > tertiary butyl > *n*-tetradecyl and *n*-dodecyl > *n*-decyl.

Through trial and error the scientists at I. G. Farbenindustrie had arrived at a schedule of addition of diproxid which gave them a rather homogeneous polymer of just about the maximal molecular weight below where gel forms readily. However, the system is not unique or inexplicable and may indeed be improved upon by using mercaptans. On the other hand, application of the knowledge obtained as to regulating index of diproxid in relation to other mercaptans would enable a similar polymer to be prepared using the Mutual formula if it were desirable. The polymer produced would be very tough and difficult to process as prepared. While such a polymer could be heat softened or degraded to a processing level well within that suitable for current factory techniques, such a step is cumbersome, costly, and, based upon reports from Europe, not easily controlled. Thus, the more suitable approach to an improved general purpose tire rubber would seem to be along the lines of lower polymerization temperatures (17, 35).

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PILOT PLANT STUDY OF GERMAN BUNA S-3 CHEMICAL RUBBER[1]

By T. L. Davies[2] and H. Leverne Williams[3]

Abstract

Buna S-3 chemical rubber was prepared in 5 and 110 gal. glass lined autoclaves. The polymerization conditions were not identical with those reported by the Germans or by a concurrent laboratory program. The polymers failed to heat soften in a manner comparable to the German material but, nevertheless, when the polymer was degraded on a mill and compounded in a standard tire tread recipe the resulting vulcanizate had properties superior to GR-S and approximating those of low temperature chemical rubber, although the Buna S-3 lacked the ease of processing of the low temperature copolymer.

Introduction

The German general purpose tire rubber, Buna S-3, although produced in a manner very similar to that used for the production of chemical rubber (GR-S) in Canada did differ both in its method of manufacture and processing. Like GR-S the I. G. Farbenindustrie product was a butadiene–styrene copolymer prepared in emulsion. The catalyst was potassium persulphate, the emulsifier was Nekal BX (isobutylnaphthalene sodium sulphonate) and the regulator or molecular weight controller was diisopropyl xanthogen disulphide (diproxid). A considerable volume of data became available following the visits of several investigators to Germany (1, 2, 3, 4, 7, 8, 9, 10, 11, 14, 15, 16, 17, 19, 20, 22, 23). Data on various copolymers prepared in this system have been published (18).

The polymer was very tough and in practice was heat softened (6) to the desired plasticity before use. In spite of this economic and processing handicap it was of interest to parallel the laboratory investigation of this polymer and the system in which it was prepared (5) by an attempt to produce larger quantities of the Buna S-3 for compounding and testing studies. When polymers produced at lower temperatures (21) were found to equal or exceed Buna S-3 in properties and were very much easier to process, the Buna S-3 program was terminated. Thus, certain questions remain unanswered by this report, which is intended to define the status of the study upon closing.

Techniques

The criterion for similarity to the I. G. Farbenindustrie product was to produce a polymer of high Mooney plasticity by the increment addition

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of diproxid regulator to maintain a horizontal intrinsic viscosity–conversion relation up to 60% conversion of hydrocarbons to copolymer.

The polymers were milled on a standard laboratory rubber mill and compounded in the standard test recipe for tire tread stocks. Unless otherwise indicated, the test methods on the vulcanizates conformed with those in use in standard testing laboratories.

Viscosities, gel, and other molecular weight data were obtained as in the previous report (5).

Experimental

Polymerization and Characterization of Polymers

Table I shows the polymerization data obtained on a large number of Buna S-3 charges in the 5-gal. reactors at 45° C.

TABLE I

POLYMERIZATION DATA

Polymer	Time, hr.	Diproxid	Conv., %	[η]	Gel, %	[η_s]	Mooney	Coagulation
T-199-4	0	0.033	0		0			
			8.5	1.7	0			
			18	2.7	0			
		0.033	25.5	3.3	0			
			31.5	3.7	0			
			37.5	3.7	0			
		0.033	44.5	4.5	5			
			53.0	0.95	78			
	32.5		56.5	2.4	63		150 L	NaCl, H_2SO_4
T-443-80	0	0.033	0					
		0.033	20	1.00	80.25			
		0.033	40	1.25	83.25			
	30.3		61.2	3.95	8.0		90 S	Alum
T-445-4	0	0.047	0					
		0.047	20	1.73	76.5			
		0.047	40	0.25	79.0			
	52.5		61.2	1.46	70.5		83 S	NaCl, H_2SO_4
T-446-1	0	0.047	0					
		0.047	20	2.75	0			
		0.047	40					
	33		60.7	4.57	7.0		95 S	Alum
T-472-3	0	0.049	0					
		0.035	20	0.55	60.8			
		0.056	40	0.68	52.2			
	33.8		69.5	1.00	68.8		88 S	Alum
T-493-2	0	0.035	0					
		0.049	20	3.05	0.75			
		0.056	40	4.7	2.5			
	30.5		59.5	2.95	12		88 S	Alum
T-525-1		0.033	20		85.0	3.5		
		0.033	40		80.8			
		0.033	60					
	48		80.8		76.5		97 S	Alum

L, Large Rotor ML/4′; S, Small Rotor MS/4′.

TABLE I—*Continued*

POLYMERIZATION DATA—*Continued*

Polymer	Time, hr.	Diproxid	Conv., %	[η]	Gel, %	[η_s]	Mooney	Coagulation
T-526-2		0.033	20		81.1	1.92		
		0.033	40		94.5	2.00		
		0.033	60		97.4	0.71		
	42.5		77		95.6	0.93	108 S	Alum
T-540-1		0.035	20		62.3	1.0		
		0.025	40		74.5	1.55		
		0.040	60					
	64.6		79.7		78.0	0.80	103 S	Alum
						0.43		
T-541-3		0.035	20		34.2			
		0.025	40		24.8	0.365		
		0.040	60					
	39.2		79		7.0	0.49	116 S	Alum
T-559-1		0.033	0					
		0.033	20					
		0.033	40					
	22.5		62.0				76 S	Alum, $FeSO_4$
T 560-1	0	0.03	0					
		0.03	20		0	2.41		
		0.03	40		8.5	3.15		
	45		51.0		8.4	2.82	90.5 S	Alum, $FeSO_4$
T-589-1	0	0.033	0					
		0.033	20		42.5	2.58		
		0.033	40		82.5	3.05		
	51		61		77.5	2.65	88 S	See Table III
T-576-1	0	0.033	0					
		0.033	20			2.10		
		0.033	40					
	48		61.8			2.24	85 S	Alum, $FeSO_4$
T-593-2	0	0.1	0					
			20		66.1	1.17		
			40		66.8	1.90		
	28		61.2		72.3	1.30	89 S	$CaCl_2$, HOAc, $FeSO_4$
T-594-2	0	0.14	0					
			20		2.5	0.67		
			40		2.5	2.35		
	33.3		60.8		65.3	1.90	70.5 S	$CaCl_2$, HOAc, $FeSO_4$
T-726-2		0.06	8			1.89		
			33			2.95		
			50			2.77		
	27		60.0			2.32	82 S	CaCl, H_2SO_4, $FeSO_4$
T-730-2		0.04	8			2.95		
			20			2.80		
			33			3.20		
			50			3.15		
	30.6		59			2.35	78 S	NaCl, H_2SO_4, $FeSO_4$
T-746-2		0.04	8			3.19		
			20			3.19		
			33			3.12		
		0.02	50			2.85		
	26		59.8			3.20		$FeSO_4$

L, Large Rotor ML/4'; S, Small Rotor MS/4'.

TABLE I—*Concluded*

POLYMERIZATION DATA—*Concluded*

Polymer	Time, hr.	Diproxid	Conv., %	[η]	Gel, %	[η_s]	Mooney	Coagulation
T-750-2		0.04	8			4.50		
			20			3.17		
			33			3.48		
		0.03	50			2.87		
	36		60.8			2.10	78.5 S	NaCl, H_2SO_4, $FeSO_4$
T-762-2		0.04	8			1.95		
			20			2.05		
			33			3.10		
		0.03	50			3.00		
	28.7		60.7			2.45	60.7 S	$FeSO_4$, NaCl, H_2SO_4

L, Large Rotor ML/4′; S, Small Rotor MS/4′.

It will be noted that the time and amount of diproxid increments were varied in an attempt to obtain a horizontal viscosity and/or vistex versus conversion curve. This was not accomplished but was being approached (see polymer T-746-2). An examination of the results in Table I indicates that a satisfactory degree of reproducibility of the Buna S-3 system with regard to conversion rate, intrinsic flow time, vistex, and Mooney has not been obtained in the Pilot Plant reactors.

The lack of reproducibility makes it difficult to evaluate the effect of varying the amount of diproxid and the time of the addition.

Polymers T-525-1, T-526-2, T-540-1, and T-541-3 were higher conversion polymers than regular Buna S-3 and Polymer T-560-1 was prepared to 50% conversion.

Heat Softening

In these experiments the polymers were placed in a hot air oven at 250° to 260° F. for a period of several hours. Samples were removed at intervals for Mooney determination. The results are shown in Table II.

Examination of the data shows that the rate of Mooney decrease for the heat softening of polymers prepared here was much lower than that of the German Buna S-3, even when the sample contained iron as catalyst. The extremely low rate of heat softening of polymers T-443-80 and T-559-1 may be attributed to the use of alum to coagulate the latex. However, variation of the coagulation system for Pilot Plant polymers has not yet produced rates of heat softening approaching that of German Buna S-3. The effect of different types of coagulation on heat softening is shown in Table III for polymer T-589-1 and at a temperature of 260° F. for a period of 30 min.

It is to be observed that coagulation with sodium chloride – sulphuric acid – ferrous sulphate mixture gave a polymer that showed a greater Mooney decrease on softening. Another important feature shown by these results is the variation in the Mooney and gel caused by different types of coagulation.

TABLE II

HEAT SOFTENING DATA

Time	Mooney *ML/4'*		
	T-443-80	*T-559-1	German Buna S-3
15 min.	—	134.5	156.5
30 "	129	136.0	135
45 "	123	—	—
60 "	119, 128	119.5	93.0
80 "	—	121.5	76
90 "	109	—	—
100 "	—	123.0	57.5
2 hr.	105, 109	123.5	51.5
3 "	99, 105	—	—
4 "	101.5	—	—
5 "	98.0	—	—
6 "	101.5	—	—
7 "	99.5	—	—
8 "	104.5	—	—
9 "	109.5	—	—
10 "	105.5	—	—
11 "	107.0	—	—
12 "	110.0	—	—

* *Coagulant for Polymer T-559-1 contained 0.12 gm. $FeSO_4 . 7H_2O$ per 100 gm. of polymer.*

TABLE III

EFFECT OF TYPE OF COAGULATION ON POLYMER

Polymer T-589-1	Coagulation type	Original gel, %	Original Mooney *ML/4'*	Final Mooney *ML/4'*
A	Alum	78.8	149.5	151.5
B	Alum + $FeSO_4$	75.0	155.0	151.0
C	Brine-acid	83.5	147.5	112.5
D	Brine-acid + $FeSO_4$	61.0	147.5	107.5
E	$CaCl_2$-HOAc	79.4	144.5	138.5
F	$CaCl_2$-HOAc + $FeSO_4$	81.2	143.0	125.5
G	NaCl-HOAc	89.5	146.0	117.0
H	NaCl-HOAc + $FeSO_4$	78.3	150.0	121.5

Mill Breakdown

The results of breakdown, on a cold mill, of some of the polymer prepared are shown in Table IV.

It is observed that although German Buna S-3 has a faster rate of mill breakdown than the Pilot Plant polymers, the deviations are not nearly as marked as they were in the heat softening data. Polymer T-213-4 during the interval 10 to 40 min. showed a greater rate of mill breakdown.

The fact that this polymer was the only one coagulated with sodium chloride–sulphuric acid may be of some significance in view of the heat softening data of Table III from which it is seen that the polymers coagulated with sodium

TABLE IV

MILL BREAKDOWN DATA

Time, min.	Mooney *ML*/4′					% Gel	
	T-213-4	T-443-80	T-525-1	T-559-1	German	T-213-4	German
0	171	158	—	131.5	161	40.9	17.4
2	174	157	—	—	160	41.5	5.4
5	173	156	112	114.0	147	39.4	0
10	170	142	106.5	93.5	127	0	0
15	146	131	99.0	83.0	102	0	0
20	120	113	84.5	76.5	93	0	0
25	—	—	—	72.5	—	—	—
30	93.5	94	—	68.5	80	0	0
40	81.5	—	59.0	60.0	72	0	0
45	—	83	—	—	—	—	—
60	—	74	—	—	—	—	—

chloride–sulphuric acid solutions showed the greatest Mooney decrease during heat softening.

Physical Test Data

Although this investigation is by no means complete, Table V illustrates some of the results obtained in examining the compounded and vulcanized sample. The polymers were compounded in the standard Rubber Reserve formula and cured at 292° F. for the times indicated.

TABLE V

PHYSICAL TEST DATA

Polymer	Mill breakdown	Cure, min.	Maximum tensile, p.s.i.	Elong., %	Modulus, p.s.i.	Cure, min.	Rebound, %	Cure, min.	Flex, in./Kc.
T-199-4	30	80	4280	650	1210	85	61.4	70	13.3×10^{-3}
T-213-4	30	90	4363	565	1708	—	—	—	—
T-443-80	15	80	4086	665	1189	—	—	—	—
T-443-80	30	85	4044	675	1175	95	59.2	80	11.3×10^{-3}
T-443-80	60	85	4071	722	1071	95	58.6	80	10.3×10^{-3}
T-443-80	90	90	3864	688	1142	—	—	—	—
German Buna S-3	40	50	4042	650	1220	—	—	—	—

Examination of the physical test data shows that faster rates of cure were obtained for the I. G. Farbenindustrie Buna S-3 samples. On an average, compounded in the standard recipe the German samples required a 50 min. cure at 292° F. for maximal tensile strength while the polymers prepared in the Pilot Plant averaged 85 min. for curing to maximal tensile strength.

Physical test data on compounded stock show very similar results, indicating, at least in this respect, that the quality of the European polymers is being approached.

Discussion

Failure to duplicate the Buna S-3 exactly in larger scale production in the Polymer Pilot Plant cannot be explained precisely. Perhaps more exact duplication of the German polymerization system, particularly the constant viscosity versus conversion relation, may solve the difficulty. A lower gel content and higher swelling index of the gel may result and alter the breakdown characteristics of the polymer. The effects of coagulation and drying on the properties of the polymer have not been investigated fully, but there is evidence that the coagulation step may alter the polymer considerably, and impurities left in the polymer from the polymerization, coagulation, or washing stage may affect the breakdown characteristics of the polymer. Most important, however, is the difference in agitation. The Germans used slow speed agitation, whereas the equipment used in the present investigation was high speed. This can alter the disappearance of regulators considerably and may make the molecular weight distribution entirely different. The high rate of diproxid disappearance normally (5) would suggest that it should not be sensitive to agitation.

In spite of this difference the properties of the polymers approached those of low temperature polymers (21) and surpassed those of GR–S (12, 13). However, the polymers would not be suitable for the usual factory procedure without heat softening to lower Mooney viscosities before compounding.

With the development of easily processed polymers of comparable quality the commercial application of this polymer must await development of either a suitable heat softening technique or suitable alteration in formula to enable easy processing.

Acknowledgments

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THE DIFFUSION OF LIGHT BY GROUND GLASS, WITH SPECIAL REFERENCE TO COLOR CHANGES[1]

By W. E. Knowles Middleton[2] and F. D. Smith[3]

Abstract

By special methods of grinding it has been found possible to make reproducible ground-glass surfaces. A series of six surfaces of increasing roughness was produced in crown glass, and a similar series in flint. These were illuminated at normal incidence by 2850° K. light in a photoelectric goniophotometer and intensity was measured at various angles. The apparent color temperature of the light diffused at each angle was also measured photoelectrically, with visual checks at some angles. Photomicrographs were taken of some of the surfaces, and finally the recording spectrophotometer was used to measure the diffuse reflectance, diffuse transmittance, and transmittance over a half-angle of about 8°, of several glasses. Some sandblasted samples were also studied. The transmitted light is most reddish at 0°, while at angles of more than 60° most of the glasses raise the apparent color temperature of the light. With the most finely ground glasses the color temperature at 0° reaches 2300° K. Some theoretical studies lead to the belief that most of the color changes are due to scattering, while diffraction plays a minor part.

Introduction

In comparison with other systems which diffuse light, whether translucent like opal glass or opaque like magnesium oxide, ground glass has received relatively little attention, either experimental or theoretical. A fairly extensive search of the literature since 1920 discloses only a few papers with quantitative significance. Reference may be made to articles by Schulz (10), Leontowitsch (6), Lax and Pirani (5), Kuhl (4), English (2), and Cohu (1). None of these contain any data on the change of color of the light, except in a very indirect way, exemplified by the curves for two wave lengths in the article by Kuhl (4).

There are probably two reasons for this neglect. In the first place, the surface of ground glass is very complex geometrically, and this renders the formulation of a rigorous theory extremely difficult if not impossible. Secondly, from the experimental standpoint, the difficulty of reproducing ground surfaces has probably discouraged elaborate measurements.

The present contribution does not pretend to provide a full theory of the diffusion of light by ground glass, though it will be shown later that diffraction alone is entirely inadequate to explain the observed phenomena. The second of the above-mentioned difficulties has, however, been surmounted, and we shall describe a method of making ground-glass surfaces that can be duplicated even after many months with satisfactory precision. The main emphasis in our work has been on the color changes, but data on the angular variation of

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luminance and the diffuse transmittance and reflectance will also be presented. It has been found that the changes in the color of the light can be adequately specified by means of the concept of color temperature, provided the incident light has the spectral distribution appropriate to a perfect radiator.

Preparation of the Ground Glass Samples

In the normal process of grinding glass, the abrasive breaks down very rapidly, and the roughness of the final surface depends to a very large extent on the rate at which new abrasive is supplied and the rate at which the finer broken down abrasive is carried away. The variation in pieces of ground glass, prepared in succession by the same workman using the same tools and procedures, might be small, but the variation between samples prepared by different workmen or in different workshops with the same abrasive undoubtedly will be quite large.

The samples of ground glass used for our measurements were prepared by a method which has been found to give reproducible results. The samples were ground by hand on a flat iron lap about 20 in. in diameter. A box 6 in. square (Fig. 1) carried a flat piece of sponge rubber on its underside. This

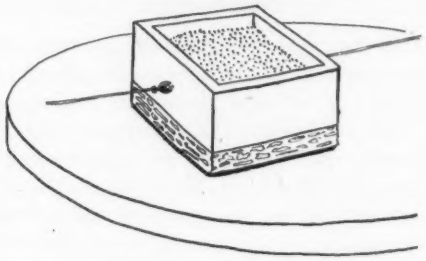

FIG. 1. *Grinding box.*

box was placed on the glass sample on the lap, and weights to give a pressure of 1 p.s.i. were added to it. Short lengths of string attached to two sides of the box were used to pull it over the surface of the lap as described below. The upper surface of the sample was protected with shellac and no serious slippage was observed.

A uniform, relatively light coating of very wet abrasive was spread on the lap and the glass drawn by means of the strings in a zig-zag fashion over the surface. A slight, rotary, to-and-fro motion with amplitude about 30° was given to the flat as it was drawn over the path. On the completion of one such "pass", as shown in Fig. 2, the lap was washed clean and the entire process repeated. The glass samples had been previously optically ground and polished, and so the time to produce a fully ground surface by the above process was reduced to a minimum. When the surface was first judged fully ground, ten extra passes were made as a safety precaution.

Samples of flint ($n_D = 1.617$) and crown ($n_D = 1.510$) glass were ground with 60, 150, and 280 mesh carborundum, 600 and 1000 mesh emery and

No. 8 garnet in decreasing order of size. The No. 8 garnet has a particle size of 8 μ. The range covered is indicated by the photomicrographs (Fig. 3) of flint samples ground with (*a*) 60 mesh carborundum, (*b*) 600 mesh emery, and (*c*) No. 8 garnet respectively. The magnification is 200 times, and the illumination by reflected light.

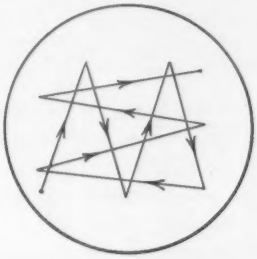

FIG. 2. *Showing motion of box in grinding.*

The General Nature of the Surfaces

As will be seen from Fig. 3, the ground surfaces appear exceedingly complex when viewed under the microscope. In every case a number of relatively large conchoidal chips have been removed, but the greater part of the surface consists of very small facets of a variety of sizes and orientations, so that the surface in this region appears to have been pounded and complex fractures can be seen. These make it appear as if scraping with some sort of sharp instrument would easily remove many of the projecting peaks of glass. The geometry of the surface appears to be the same for all the abrasives used. Thus with suitable magnification one of the surfaces ground with emery can be made to appear indistinguishable from one of the coarser carborundum-ground surfaces. The sandblasted samples were very similar to ground samples of corresponding roughness, except that the large conchoidal fractures were less numerous and relatively smaller, while the surface as a whole undulated slightly and made it difficult to bring a large area in focus at once under the microscope. This similarity in appearance between the ground and sandblasted samples may, as Preston (9) has suggested, result from the fact that the two processes are pounding processes and fundamentally the same.

Experimental Methods

Most of the measurements were made with the sample illuminated by a simple gonio-illuminator mounted on an optical bench. This apparatus, which presents no novel features, made it possible to illuminate the sample with a collimated beam at any angle of incidence, and to observe it from any angle of view in the plane of incidence, though not closer than about 20° to the direction of the beam on the incident side. The half-angle of divergence of the beam in the plane of incidence was about 1.7°. For most of the observations, a photoelectric photometer was used, fitted with filters for the measurement of color

temperature; but checks were also made by direct visual comparison in a Lummer-Brodhun photometer with a magnesium oxide screen illuminated by a sub-standard of color temperature. All the measurements were made with incident light having a color temperature of 2850° K. (I.C.I. source "A"), and nearly all at normal incidence.

In addition to the goniophotometric measurements, a recording spectrophotometer was used to measure the singly diffuse transmittance and reflectance of the samples, and also the transmission in a cone of half-angle about 8°.

Measurement of Intensity, Luminance, and Color Temperature

A photocell (R.C.A. type 926) was mounted permanently at one end of the optical bench. In front of the cell was a slit about $\frac{1}{8}$ in. wide, backed by a paper diffusing screen. This arrangement was left unaltered throughout the experiments, including calibrations.

For measurements of the angular distribution of intensity, a mask with an aperture $\frac{1}{4}$ in. wide and 1 in. high, cut in thin sheet metal, was placed in contact with the ground surface of the sample. A fixed distance from glass to cell was used. The calibration of the photocell and its associated circuits was carried out with the aid of the optical bench and a lamp run on controlled voltage. The luminance of the ground-glass surface was not measured directly, but was calculated by dividing the intensity by the cosine of the angle of view.

The measurement of color temperature was carried out by measuring the relative response of the photocell when two filters, one red and the other blue, were separately placed in front of it. A color temperature sub-standard lamp and a magnesium oxide screen were used for calibration. In order to define the illuminated area, a mask with a $1\frac{1}{2}$ in. diameter opening was placed in contact with the sample. By varying the distance from sample to photocell, and by the use of an auxiliary adjustable slit, it was easy to perform all the measurements, including calibration, at about the same level of photocell output. The angle of view was in all cases less than the angular divergence of the incident beam.

It has been pointed out by various authors (7, 12) that this way of measuring color temperature tacitly assumes that the spectral distribution of the light is similar to that of a black body. For this reason it was felt to be necessary to make some visual comparisons between the color of the light from the ground glass and of that from a magnesium oxide screen illuminated by a color temperature sub-standard; this was done by modifying a Lummer-Brodhun photometer by the addition of inclined mirrors (11, p. 209). As will be shown below, the results of these measurements (and of spectrophotometric determinations) support the validity of the photoelectric method.

Results

Angular Distribution of Luminance

It is felt to be more useful to state the angular distribution of luminance than of intensity, because this facilitates comparison with a perfect diffuser,

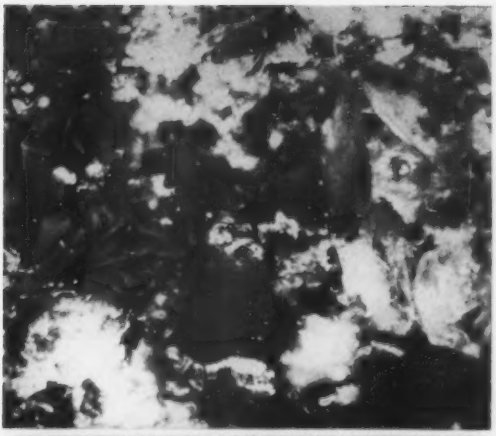

FIG. 3 (*a*)

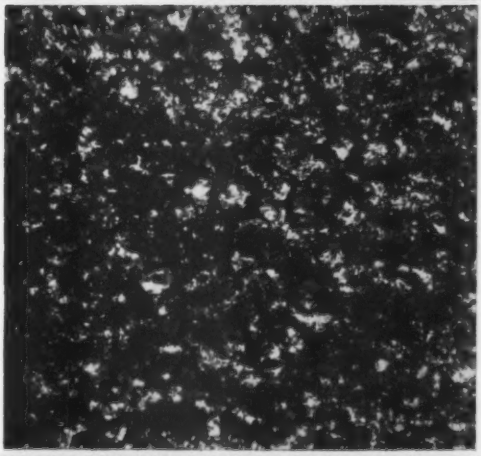

FIG. 3 (*b*)

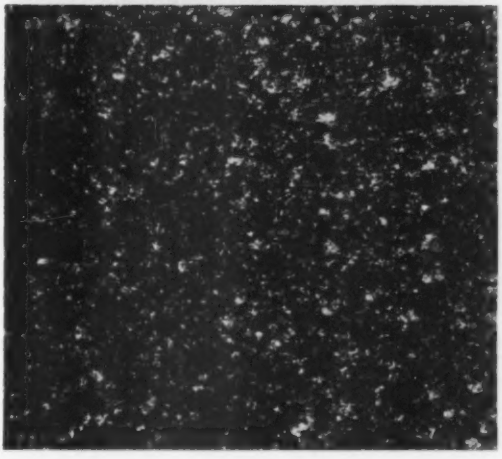

FIG. 3 (*c*)

FIG. 3. *Photomicrographs of ground surfaces (×200) by reflected light.*

the luminance of which is the same at all angles. The curve for the perfect diffuser would appear as a horizontal straight line in this method of plotting.

In Fig. 4 we present data for three different grinds of crown glass, including the coarsest and the finest; and it will at once be seen that there is little difference in their diffusing power. All the curves in Fig. 4 refer to light incident

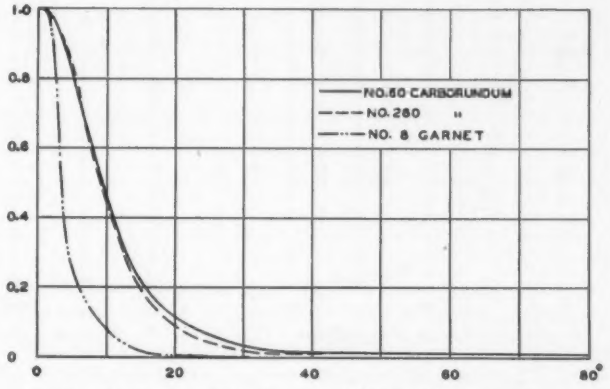

FIG. 4. *Angular distribution of luminance. Light incident normally on ground side. Crown glass, grinds No. 60, No. 280, and No. 8.*

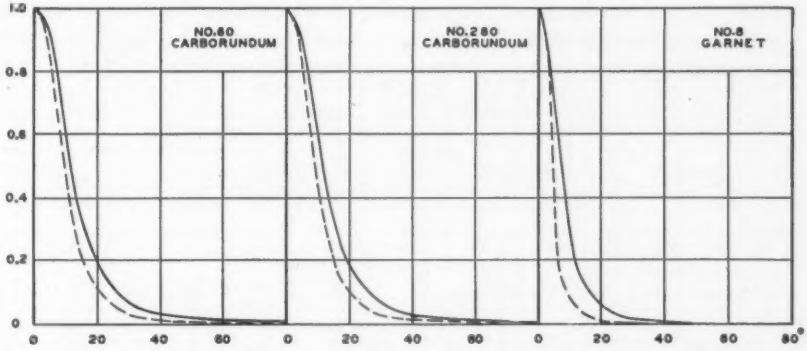

FIG. 5. *Angular distribution of luminance. Light incident normally on ground side. Solid curves—flint glass. Broken curves—crown glass.*

on the ground side, as do those of Fig. 5, which compare crown and flint glass. The flint glasses are notably better diffusers, an important practical consideration.

There is a small but interesting difference (Fig. 6) between the results for incidence on the ground side and on the polished side. The latter orientation leads to about twice the luminance at very large angles, presumably because a good deal of the back-reflected light from the ground side is incident internally on the polished side at more than the critical angle, and is totally reflected.

Even sandblasted glasses present much the same appearance (Fig. 7). This figure shows clearly the much greater importance of the type of glass than of the particular details of sandblasting technique.

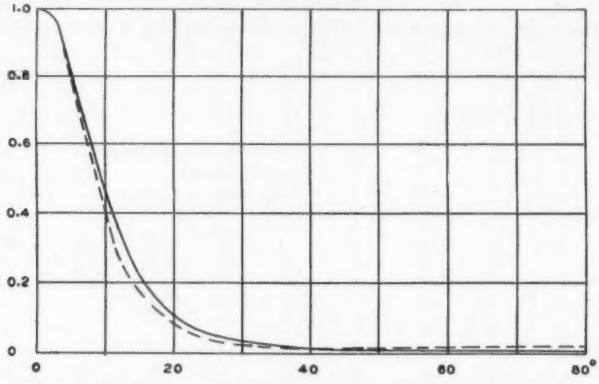

FIG. 6. *Angular distribution of luminance. Crown glass, No. 60 grind. Solid curve—light incident on ground side. Broken curve—light incident on polished side.*

All the curves, both for ground glass and for sandblasted, can be fitted quite well to a Gaussian curve of error at angles below about 15°.

Table I gives the values of the angles of view at which the brightness falls to one-half and one-tenth of the value at 0°. In every case the light is incident on the rough side.

TABLE I

Abrasive	Crown glass		Flint glass	
	θ for $B=0.5B_0$	θ for $B=0.1B_0$	θ for $B=0.5B_0$	θ for $B=0.1\ B_0$
Ground glasses				
60 mesh carborundum	9.5°	21.1°	11.4°	26.7°
150 mesh carborundum	9.6	21.9	—	—
280 mesh carborundum	9.3	19.5	11.6	25.0
600 mesh emery	8.6	17.7	9.4	22.1
1000 mesh emery	6.4	14.1	8.8	19.9
No. 8 garnet	4.4	8.5	6.4	15.9
Sandblasted glasses				
200/40	9.6	22.0	12.5	29.1
200/70	9.7	23.0	—	—
100/40	10.1	23.6	—	—
100/70	10.9	24.5	14.2	32.1

The sandblasted samples are evidently somewhat more effective diffusers, although in appearance they have the roughness of glass ground with about 150 mesh carborundum. It is also noted that all samples of a given glass ground with carborundum are very similar in their diffusion properties in spite of a wide range (about 5 to 1) in coarseness.

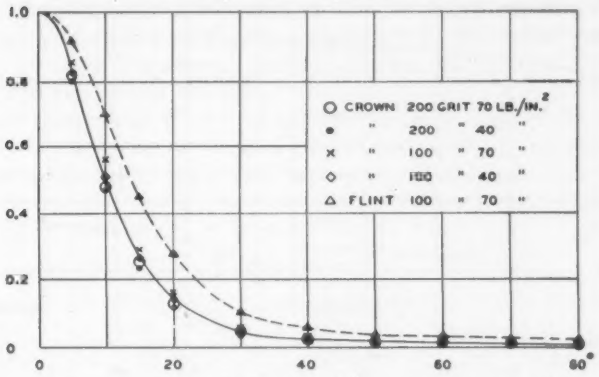

FIG. 7. *Angular distribution of luminance, sandblasted samples.*

Color Temperature Changes

Some of the results of the photoelectric color temperature measurements are shown in Figs. 8 and 9 for crown and for flint glass, illuminated by 2850° K. light incident normally. In every instance the transmitted light is reddest at small angles of view, but it will be noted that the change in color is less marked for the rougher surfaces. The great lowering of the color temperature at low

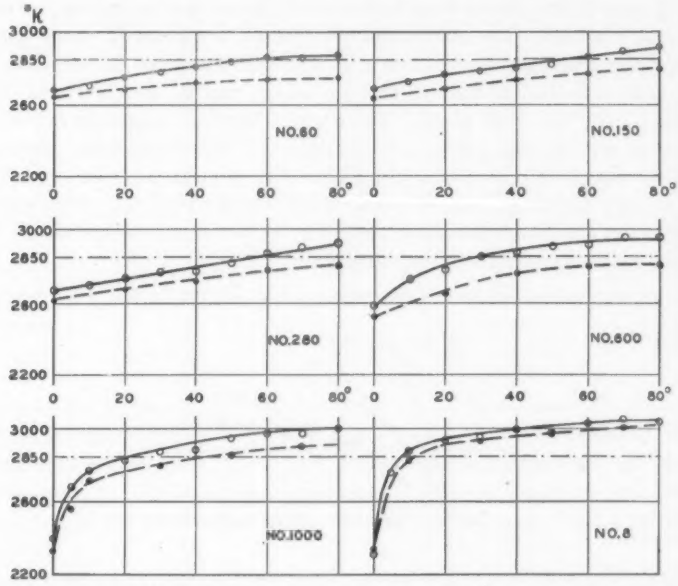

FIG. 8. *Change of color temperature with angle of view. Crown glass, 2850° K. light incident normally. Solid curves—incident on ground surface. Broken curves—incident on polished surface.*

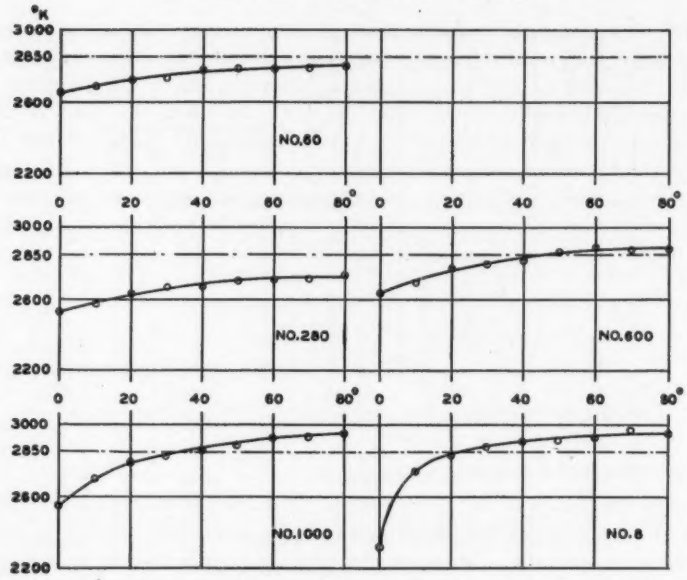

FIG. 9. *Change of color temperature with angle of view. Flint glass, 2850° K. light incident normally on ground surface.*

angles of view in the case of finer surfaces is believed due to scattering; this will be discussed below. The curves for flint glasses are lower in every case than those for the corresponding crown samples, and this may be ascribed to the loss by total reflection of light of shorter wave lengths, which would be more pronounced for the flint glass. The curves for flint glass are all for light incident on the ground surface. The angle at which the color temperature is equal to that of the incident light (2850° K.) can be read from Figs. 8 and 9. It varies fairly systematically with the coarseness of the grind. When the light is incident on the ground surface the color temperatures observed are higher, as shown by the curves for crown glass (Fig. 8).

This higher value of color temperature can be explained by reference to

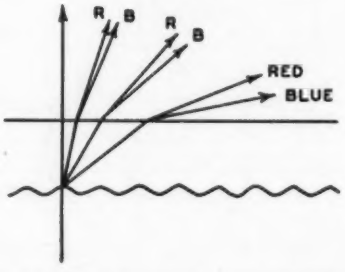

FIG. 10. *Diagram showing probable mechanism producing the difference between the two sets of curves in Fig. 8.*

Fig. 10. If we suppose that the color of light leaving the rough interface at a given angle is the same for the two cases, then for incidence on the rough surface, refraction at the second, polished, surface will cause a further spectrally selective diffusion of the light. One would expect the color to be only very slightly changed at 0° and to have a maximum change at the largest angle. The fact that the curves show an increase in the effect with angle of view supports this explanation, and total reflection will also take place at a smaller angle for the shorter wave lengths. However, some other process must operate to produce the effect near 0°.

Visual Measurements of Color Temperature

Visual measurements of color temperature were later made by the method described above (p. 154). The values (Table II) so obtained tended to be slightly lower than those obtained photoelectrically, but, except for light at small angles from finely ground surfaces, the difference was never greater than 35° K. and in most cases 20° K. or less. The larger (and positive)

TABLE II

COLOR TEMPERATURE CHANGES OBTAINED VISUALLY AND PHOTOELECTRICALLY. LIGHT (2850° K.) INCIDENT ON GROUND SIDE

Glass sample	θ, degrees	CT observed visually, T_V	CT observed photo-electrically, T_P	Difference $T_V - T_P$
No. 60 Crown	10	2670	2700	−30
	20	2745	2750	− 5
	30	2850	2780	−30
	40	2790	2800	−10
	60	2835	2855	−20
No. 280 Crown	10	2685	2700	−15
	20	2790	2720	−20
	30	2745	2765	−20
No. 600 Crown	0	2550	2580	−30
	10	2700	2710	−10
	20	2755	2790	−35
	40	2915	2890	+25
	60	2925	2935	−10
No. 8 Crown	0	2350	2305	+45
	5	2800	2760	+40
	10	2870	2880	−10
	20	— intensity too low for match.		

discrepancies (up to 45° K.) for the finely ground samples probably resulted from the circumstance that the included angle was somewhat greater (up to 4°) than that used for the other measurements. Thus it would be expected from the steepness of the curve in the region near $\theta = 0°$ that too high a value would be obtained.

It is important to record here that a satisfactory match was obtainable in every instance, a fact which justifies the employment of the concept of color temperature to specify the color of the light transmitted by these glasses.

Spectrophotometric Measurements

Measurements with the recording spectrophotometer indicate that the colors of the transmitted light are very close to the Planckian locus. Some of the resulting colors, calculated from the diffuse spectral transmittances, are shown in Fig. 11, and from spectral transmittances in an 8° cone in Fig. 12. It

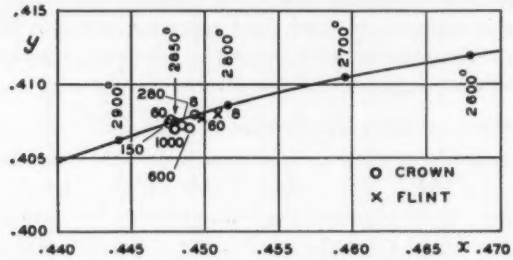

FIG. 11. *Portion of the I.C.I. chromaticity diagram, showing calculated chromaticities of diffusely transmitted light from a 2850° K. source, and also a portion of the Planckian locus. Light incident on ground side.*

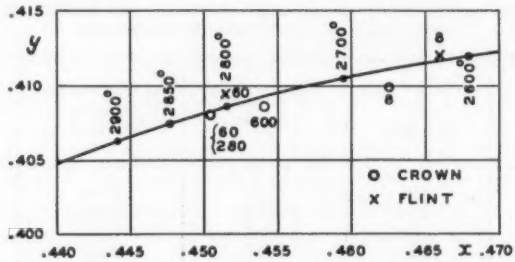

FIG. 12. *Portion of the I.C.I. chromaticity diagram, showing calculated chromaticities of light from a 2850° K. source transmitted in a cone of 8° half-angle. Light incident on ground side.*

should be noted that the spectrophotometric results are for geometrical conditions very different (regarding collection of light) from the photoelectric results. The color of the transmitted light is scarcely changed from that of the incident light if all the transmitted light is collected (Fig. 11); but the light in the 8° cone is distinctly redder, the more finely ground glasses changing the color more. It is probably not significant that the points for the four crown glass samples lie on the purple side of the Planckian locus, while the flint glass samples are on the green side, since the displacements are not much more than the experimental errors.

Diffuse reflectance* was also measured with the spectrophotometer and again the colors, more bluish in this case, were close to the Planckian locus.

Reproducibility of Ground Surfaces

A comparison of Figs. 8 and 9 will disclose the absence of grind No. 150 from the series of flint glass samples. Two samples of glass, supposed to be

* *The sample backed by a hollow blackened enclosure.*

crown and flint, had been ground with 150 mesh carborundum, and when they were tested in the goniophotometer they proved to be identical within the error of the experiments. A refractometer showed that they were in fact both crown glass, $n_D = 1.510$. These were, of course, prepared at about the same time in June, 1947. To determine whether samples could be reproduced after the lapse of a year, samples of No. 600 crown and No. 280 flint were prepared in the summer of 1948, and compared with the 1947 samples. The measurements of color temperature and luminance agreed almost within the errors of the experiment (Tables III and IV). Spectrophotometric measurements

TABLE III

REPRODUCIBILITY OF COLOR TEMPERATURE

θ, degrees	Color temperature, °K.		
	1948	1947	Difference, 1948 − 1947
Crown No. 600			
0	2610	2585	+25
10	2690	2705	−15
20	2760	2780	−20
30	2830	2850	−20
40	2920	2890	+30
50	2930	2920	+10
60	2945	2940	+ 5
70	2970	2930	+40
80	2965	2950	+15
Flint No. 280			
0	2620	2645	−25
10	2680	2685	− 5
20	2760	2740	+20
30	2785	2770	+15
40	2800	2780	+20
50	2800	2810	−10
60	2810	2815	− 5
70	2845	2820	+25
80	2860	2840	+20

suggest that the variation from point to point on one sample is of the same general magnitude as the difference between samples.

It should, of course, be mentioned that nearly all our samples were approximately the same size, about 3 × 3 in., though one or two were smaller. While no experiments have been made on this point, it seems likely that similar results would be obtained with samples of various sizes as long as the pressure was kept the same. It is regretted that this question was overlooked when the experiments were under way.

TABLE IV

REPRODUCIBILITY OF LUMINANCE DISTRIBUTION

θ, degrees	Relative luminance			
	Crown No. 600		Flint No. 280	
	1948	1947	1948	1947
0	1000	1000	1000	1000
5	772	767	880	872
10	389	385	570	566
15	150	151	312	315
20	67	70	166	169
30	20	19	52	55
40	8	8	23	23
50	5	5	14	14
60	4	4	5	7
70	3	4	2	4
80	3	3	1	2

Theoretical Considerations

A theoretical explanation of diffusion by ground glass must take into account the effect of refraction, diffraction, and scattering. The experimental results however, as well as theoretical investigation, show unquestionably that refraction plays by far the largest part.

It is quite evident that an air–glass interface consisting of small facets at various angles to the normal would cause a general deviation of normally incident light, both by refraction and reflection, which would be more effective for the shorter wave lengths. Thus the light transmitted through such a surface and observed at large angles to the normal would be more bluish than the incident light. If the light is incident on the polished surface and if only a single refraction takes place for each ray, the color of light observed at 0° will be the same as that of the incident light. It is, however, quite evident that there must be multiple reflection and refraction for many of the rays passing through the surface. Some of the light observed at 0° will have undergone such a process, and since the diffusion is away from the direction of incidence and is more effective for the shorter wave lengths, we should expect therefore in any small cone of rays about the normal, an increase in the proportion of light of longer wave length. This would also mean that light reflected from the surface should be somewhat bluer than that of the source. In the case of incidence on the ground surface, we should expect that diffusion would be enhanced by the refraction effect at the second, polished, surface, causing further diffusion (Fig. 10). As previously discussed, the combination of both these effects tends to give a generally lower temperature for light transmitted at large angles, in the case where the light is incident on the polished surface. On a refraction theory, the change in color should, for a given surface geometry, be the same regardless of the degree of roughness of the surface. Furthermore, these effects should all be greater for glass of higher index of refraction.

These phenomena were all observed, and from a qualitative point of view it seems certain that most of the diffusion is due to refraction.

We may attempt a numerical evaluation of the contribution of single refractions if we consider the entire surface of the glass to be made up of a large number of prisms of all possible angles. We shall confine our discussion to incidence on the polished side of the sample. To render the problem definite, we must choose a distribution function of some sort, and it seems logical to select a probability function. Let us assume, therefore, that the projected area of surface having a slope between $\phi - \frac{1}{2}d\phi$ and $\phi + \frac{1}{2}d\phi$ is given by:

$$ds = Ae^{-h^2z^2}dz, \tag{1}$$

where

$$z = \tan \phi. \tag{2}$$

In other words, let the distribution of tan ϕ follow a probability function. It may easily be shown (Fig. 13) that

$$\tan \phi = \frac{\sin \theta}{n - \cos \theta}, \tag{3}$$

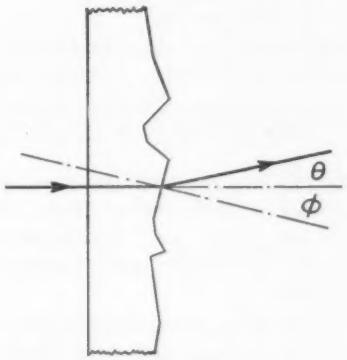

FIG. 13. *Illustrating refraction theory.*

where n is the index of refraction of the glass and θ is any angle of observation, and if we consider the flux within the conical shell defined by $d\theta$, and corresponding to $d\phi$, we obtain

$$dF = K_1 E ds = K_1 EA \frac{n \cos \theta - 1}{(n - \cos \theta)^2} \exp\left[\frac{-h^2 \sin^2\theta}{(n - \cos \theta)^2}\right], \tag{4}$$

where E is the illuminance, and K_1 takes care of losses by absorption and reflection, supposed small and independent of ϕ. For the intensity we then obtain

$$I = \frac{dF}{d\omega} = KE \frac{n \cos \theta - 1}{(n - \cos \theta)^2 \sin \theta} \exp\left[\frac{-h^2 \sin^2 \theta}{(n - \cos \theta)^2}\right], \tag{5}$$

where

$$K = \frac{K_1 A}{2\pi}.$$

The choice of h must be made from the experimental results. If we take a mean value for n we may choose h to make the intensity curve fit at any point we wish. Fig. 14 shows the result of doing this at the point where the intensity has fallen to one tenth. The theory fits the experimental curve

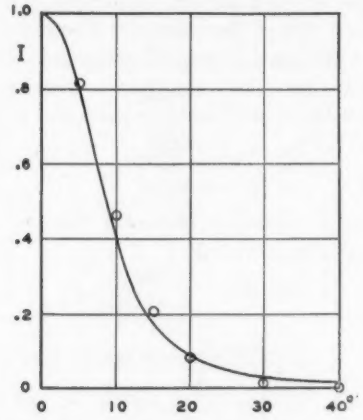

FIG. 14. *Intensity vs. angle of view. Crown glass, No. 60 grind, light incident on polished side. Circles show result of simple refraction theory; solid line denotes experimental results.*

quite well out to about 20°, but of course it cannot be expected to be satisfactory at high angles of view near the critical angle, where multiple reflections must be involved to give any light at all. This is for a coarsely ground glass. For the very fine glasses, the fit is not as good, though it is certain that refraction still plays the major role.

We do not wish to claim too much for this simple analysis. Nevertheless, in our opinion it seems probable that most of the diffusion at medium angles is produced in this way, and a probability distribution of slopes may not be far from the truth. An attempt was made to calculate the distribution of color temperature on the basis of this theory, using Hartmann's dispersion formula (3, p. 115) for n; but the amount of computation required turns out to be unjustifiably great.

It is quite obvious, at any rate, that the change of color temperature at 0° cannot be explained by a theory depending solely on refraction. The results shown in Figs 8 and 9, in which the reddening of the light at small angles is seen to depend mainly on the fineness of the grinding, make it most likely that this is a pure scattering phenomenon. A further investigation of the polarization phenomena, which should accompany this, is desirable.

The third possible mechanism of diffusion is diffraction by the small irregularities of the glass, considered as obstructing bodies.

On a diffraction theory one should expect a marked change in color with the coarseness of the grind. This was not observed with the rougher surfaces,

but was very evident with the very fine surfaces. On the other hand, little change should occur between crown and flint samples if diffraction is the main cause of the effect; but marked differences did occur, which were larger than could be attributed to the difference in roughness for a given abrasive due to the difference in hardness of the two glasses. (The flint samples are somewhat coarser than those of crown because the glass is somewhat softer, though the difference is considerably less than the steps of roughness between successive grades of abrasive). Furthermore, the diffraction does not explain the increased redness observed at low angles of scattering, for according to this theory the color at 0° should be the same as that of the source, becoming redder as the angle of view increases. Nevertheless, it was thought desirable to estimate the contribution of diffraction to the intensity at various angles.

Consider the ground surface of the glass to be made up of a very large number of circular obstructing particles, of various radii r, and in numbers distributed according to the law

$$P(r) = A^{-h^2(r-r_0)^2}. \tag{6}$$

If we direct our attention only to the particles of some one radius r, we can apply the theory of the corona (8, p. 470). Let there be P particles of radius r, and observe them from an angle θ to the direction of the incident light; then the flux per unit solid angle in the direction θ is

$$I = EP\pi^2r^4\left[1 - \frac{1}{2}\frac{m^2}{1} + \frac{1}{3}\frac{m^4}{(1.2)^2} - \frac{1}{4}\frac{m^6}{(1.2.3)^2} + \cdots\cdots\right]^2, \tag{7}$$

in which

$$m = \frac{\pi r \sin\theta}{\lambda},$$

where λ is the wave length of the light. Tables of I as a function of m are available (8, p. 479) for $P = 1$.

If we keep λ and θ constant, we may calculate I as a function of r, and then let r vary, integrating mechanically to obtain

$$I_{\lambda\theta} = \int_0^\infty F(r) \cdot P(r)dr. \tag{8}$$

This procedure was carried out for a distribution of particles with a mean radius r_0 (Equation 6) of 2μ, and a value of h such that the number of particles of radius 20 μ is 1/100 of the number of radius 2μ. This is a very fine grind. Using a wave length of 550 mμ, the intensity at $\theta = 3°$ was found to have fallen to about 1/30 of that at $\theta = 0°$, and to less than 1/100 at $\theta = 6°$. This may be compared with any of the curves of Figs. 5 to 7. Other distributions of particle sizes cannot materially improve the result, and it must therefore be concluded that diffraction plays a minor part in the process even with the more finely ground surfaces. This conclusion was also reached by Leontowitsch (6), who endeavored to explain the phenomenon on the basis of the electromagnetic

theory of light. He found that diffraction was an adequate explanation only for very fine, almost invisible surfaces.

Summarizing our theoretical findings, we may say that refraction, scattering, and diffraction contribute in that order to the total diffusion of light by ground glass, with refraction playing by far the largest part.

Conclusion

In this paper we have presented a method of making reproducible ground-glass surfaces, and also the results of measurements of the light transmitted by ground and sandblasted glass at various angles, in particular of the color temperature of the light. An attempt has also been made to give an elementary theoretical account of the phenomenon.

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THE MECHANICAL BEHAVIOR OF GUY WIRES[1]

By J. W. Campbell[2]

Abstract

The general manner in which guy wires behave is well known, but in this paper the problem is treated by means of new catenary formulae which are especially convenient for the purpose. The behavior is discussed in detail, and there is given a simple practical means of designing a set of guy wires which will serve any preassigned purpose. The method is illustrated by numerical examples.

Introduction

When a column is supported by a set of guy wires each wire hangs in the form of a catenary. The wires each exert a lateral force on the column, and when the column is vertical these lateral forces balance one another. Then when a lateral external pressure is exerted on the column, by wind, for example, the column must sway. The sway will increase the tensions of the wires on one side and decrease the tensions on the other side. The increase will exceed the decrease and the sway of the column will increase until equilibrium is established with the external pressure.

There will also be an absorption of energy which will re-establish the column to the vertical position when the external pressure ceases.

If the wires are pulled to too high a tension in the vertical position the tensions arising from an extreme external pressure may be the maximum allowable, and if they are not taut enough the column will experience too great a sway before a sufficient restoring force is built up.

The Behavior of a Single Wire

We let the positions of the lower and upper ends be (0, 0) and (x, y). We also let T be the tension at the upper end, H the horizontal tension, s the length of the wire, and w the weight per unit length.

Then we have the relations (2, p. 248)

$$y = x \sinh k' \frac{\sinh u}{u} \tag{1}$$

$$s = x \cosh k' \frac{\sinh u}{u} \tag{2}$$

$$T = \frac{wx}{2} \frac{\cosh (k' + u)}{u} \tag{3}$$

$$H = \frac{wx}{2u} \tag{4}$$

$$y/s = \tanh k' . \tag{5}$$

[1] *Manuscript received August 19, 1948.*

Contribution from the Department of Mathematics, University of Alberta, Edmonton, Alberta.

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The k' and u are parameters, and their meanings may be taken as given by Equations (4) and (5).

When the column sways, x varies but y may be taken as constant. In fact all the symbols in these equations vary except y and w, although the variations of some are more appreciable than those of others. The variations of s and k', for example, are slight.

FIG. 1

We shall designate by subscripts 1 and 2 the values of these varying symbols without and with sway. Then we have the relations:

Without sway		With sway	
$y = x_1 \sinh k_1' \frac{\sinh u_1}{u_1}$	(6)	$y = x_2 \sinh k_2' \frac{\sinh u_2}{u_2}$	(11)
$s_1 = x_1 \cosh k_1' \frac{\sinh u_1}{u_1}$	(7)	$s_2 = x_2 \sinh k_2' \frac{\sinh u_2}{u_2}$	(12)
$T_1 = \frac{wx_1}{2} \frac{\cosh (k_1' + u_1)}{u_1}$	(8)	$T_2 = \frac{wx_2}{2} \frac{\cosh (k_2' + u_2)}{u_2}$	(13)
$H_1 = \tanh k_1'$	(9)	$H_2 = \tanh k_2'$	(14)
$y/s_1 = \tanh k_1'$	(10)	$y/s_2 = \tanh k_2'$	(15)

The restoring horizontal force arising from the sway and due to this wire is therefore

$$\frac{w}{2}\left(\frac{x_2}{u_2} - \frac{x_1}{u_1}\right), \tag{16}$$

and the moment of this restoring force about the base is

$$\frac{wy}{2}\left(\frac{x_2}{u_2} - \frac{x_1}{u_1}\right). \tag{17}$$

There is another relation, involving the modulus of stiffness of the wire. Denoting that modulus by λ we have

$$T = \lambda \frac{s - s_0}{s_0}, \tag{18}$$

where s_0 is the unstretched length.

Then

$$s_2 = s_1 + \frac{T_2 - T_1}{\lambda} s_0 ,$$

and since λ is large and $s_1 - s_0$ is small, no appreciable error will be involved if we write

$$s_2 = s_1 + \frac{T_2 - T_1}{\lambda} s_1 . \tag{19}$$

The Energy Absorbed in the Sway

The energy absorbed will arise from two sources, viz., the work done by the horizontal force H in varying x, and the work done by T in stretching the wire.

The first of these is

$$\int_{x_1}^{x_2} H\, dx .$$

Now from Equation (1)

$$x = \frac{y}{\sinh k'} \frac{u}{\sinh u} ,$$

whence

$$dx = \frac{y}{\sinh k'} d\left(\frac{u}{\sinh u}\right) ,$$

if we neglect the variation of k'.

Therefore

$$H\, dx = \frac{wx}{2u} dx = \frac{wy^2}{2 \sinh^2 k'} \frac{1}{\sinh u} d\left(\frac{u}{\sinh u}\right) ,$$

and

$$\int_{x_1}^{x_2} H\, dx = \frac{wy^2}{2 \sinh^2 k'} \left[\frac{1}{\sinh u} \frac{u}{\sinh u} - \int \frac{u}{\sinh u} d\left(\frac{1}{\sinh u}\right)\right]_{u_1}^{u_2}$$

$$= \frac{wy^2}{8 \sinh^2 k'} \left[\frac{2u - \sinh 2u}{\sinh u}\right]_{u_1}^{u_2} .$$

Since the tension varies linearly as the stretch it follows that the energy absorbed in stretching the wire is

$$\frac{1}{2} (T_1 + T_2) (s_2 - s_1) .$$

Therefore the total energy absorbed in the sway is

$$\frac{wy^2}{8 \sinh^2 k'} \left[\frac{2u - \sinh 2u}{\sinh u}\right]_{u_1}^{u_2} + \frac{1}{2} (T_1 + T_2) (s_2 - s_1) . \tag{20}$$

Method of Solution

If y, x_1, x_2, u_1, and w are given we may proceed in the following manner:

(1)′ By means of (6) find k_1'.

(2)′ For a first approximation put $k_2' = k_1'$ in (11) and find u_2.

(3)′ Find T_1 and T_2 from (8) and (13).

(4)′ Find s_1 from (7) and then find s_2 from (19).

(5)′ From the result of (4)′ and (15) find k_2', second approximation.

(6)′ Repeat (2)′ to (5)′ until no further change in k_2' occurs.

The values of the restoring force, restoring couple, and the energy absorbed may then be calculated.

This is a general solution, but in practice it admits of simplification in most cases. For the λ is usually so large that no appreciable effect is afforded by (19). A variation of T which would make the effect of (19) appreciable would put the tension beyond the breaking point. Then both s and k' will be unchanged and (1)′ and (2)′ give the solution.

There is, however, an important technique of solution.

Technique of Solution

Instead of solving (6) for k_1', we may take the ratio of (11) to (6) and obtain

$$\frac{\sinh u_2}{u_2} = \frac{\sinh u_1}{u_1} \div \frac{x_2}{x_1}$$

Now x_2/x_1 is nearly 1, and denoting it by $1 + a$ then a is small. Also, $(\sinh u)/u$ is greater than 1 but not greatly different from 1.

Then

$$\frac{\sinh u_2}{u_2} = \frac{\sinh u_1}{u_1} \div (1 + a) .$$

This is a convenient form for numerical work.

For example, suppose that a column were guyed by cables running from the ground at 50 ft. from the foot of the column to a point 70 ft. high on the column. Suppose the cable were installed so that when the column was vertical the parameter $u = u_1$ was 0.2025 and that the cables weighed 1.55 lb. per ft. Consider the effect on two opposing cables of a sway which would move the point of attachment by 0.006×50 ft. in their plane.

For each cable we should have, with forces in lb._w and lengths in ft.,

$$\frac{\sinh u_1}{u_1} = 1.00685, \quad H_1 = \frac{wx_1}{2u_1} = \frac{1.55 \times 50}{2 \times 0.2025} = 191 .$$

For the one with span increased we should have

$$\frac{\sinh u_2}{u_2} = 1.00685 \div 1.00600 = 1.00085,$$

$$u_2 = 0.0715,$$

$$H_2 = \frac{wx_2}{2u_2} = \frac{1.55 \times 50 \times 1.006}{2 \times 0.0715} = 545 .$$

For the one with span decreased we should have

$$\frac{\sinh u_2}{u_2} = 1.00685 \div 0.994 = 1.00685 \times 1.00604 = 1.01291,$$

$$u_2 = 0.2778,$$

$$H_2 = \frac{1.55 \times 50 \times 0.994}{2 \times 0.2778} = 138.$$

The restoring force on the column by these two cables would therefore be 545 − 138 = 407 lb.$_w$, and its moment about the base would be 407 lb.$_w$ × 70 ft. = 28,490 ft. lb.$_w$.

For each one*

$$\sinh k' = \frac{70}{50} \div 1.00685 = 1.392,$$

$$k' = 1.133.$$

Therefore the tension of the one with increased span is

$$545 \cosh (1.133 + 0.072) = 545 \times 1.818 = 990 \text{ lb.}_w$$

Method of Application to Practical Problems

This illustration suggests a practical means of adjusting a set of cables when they are set up, in order to serve a designed purpose.

Suppose, for example, that the y, x_1, and w have been chosen, and that it is desired to adjust the cables (find the value of u_1) so that a pair of opposing cables will, in extreme conditions, afford a restoring moment N about the base without the tension of either cable exceeding a limit P.

We proceed as follows:

Take u_2 and u_3 as the parameters of the opposing cables at extreme sway. Find u_2 with $x_2 = x_1$ and $T = P$, since the variation in x is small.

From the tables (1, Table XVII) read

$$\frac{\sinh u_2}{u_2} = 1 + b_2 . \tag{21}$$

Then

$$\frac{wx_3}{2u_3} = \frac{wx_2}{2u_2} - \frac{N}{y}, \quad u_3 = \frac{wx_1}{2} \div \left(\frac{wx_1}{2u_2} - \frac{N}{y}\right). \tag{22}$$

From the tables read

$$\frac{\sinh u_3}{u_3} = 1 + b_3 . \tag{23}$$

Then

$$1 + a = 1 + \frac{b_3 - b_2}{2}, \tag{24}$$

and

$$\frac{\sinh u_1}{u_1} = 1 + \frac{b_2 + b_3}{2}. \tag{25}$$

** Seeing that k′ does not change in value in our solution we may for convenience drop the subscript.*

Alternatively, the maximum tension P might have been specified and the maximum sway c at the height y.

Then u_2 is determined with $x_2 = x_1$ and $T = P$, and b_2 is given by(21). Also,

$$a = c/x_1 . \tag{26}$$

Therefore

$$\frac{\sinh u_1}{u_1} = 1 + b_2 + c/x_1 , \tag{27}$$

whence u_1 is determined.

Likewise

$$\frac{\sinh u_3}{u_3} = 1 + b_2 + 2c/x_1 , \tag{28}$$

whence u_3 is determined.

Then the resisting moment about the base is

$$\frac{wx_1y}{2}\left(\frac{1}{u_2} - \frac{1}{u_3}\right) . \tag{29}$$

If this resisting moment is not sufficiently great it can be increased by increasing some or all of w, x_1, and y.

Application

Problem

It is proposed to support a column by a set of four guy wires anchored to the ground 60 ft. from the base and attached to the column 80 ft. from the ground. What should be the setting parameter of the cables if a tension of 1800 lb.$_w$ is not to be exceeded and an extreme resisting moment about the base of 60,000 ft. lb.$_w$ is to be provided, assuming the cables to weigh 1.85 lb. per ft.? What will be the extreme sway at the 80 ft. level (1) if the extreme external pressure is experienced in the plane of two of the wires, and (2) if the direction of external pressure bisects the angle between the two planes of wires?

Solution

With forces in lb.$_w$ and lengths in ft., we are given

$$x_2 = x_1 = 60, \quad y = 80, \quad P = 1800, \quad N = 60{,}000, \quad w = 1.85.$$

From (1) and (3),

$$\sinh k_2' = \frac{y}{x_2} \div \frac{\sinh u_2}{u_2}, \quad u_2 = \frac{wx_2}{2P}\cosh (k_2' + u_2) ,$$

and we solve by successive substitution.

$$\frac{y}{x_2} = 1.3333, \quad \frac{wx_2}{2P} = \frac{1.85 \times 60}{2 \times 1800} = 0.0308.$$

Approx.	u_2	$(\sinh u_2)/u_2$	$\sinh k_2'$	k_2'	$k_2' + u_2$	$\cosh (k_2' + u_2)$	u_2
1	0	1.00000	1.3333	1.0984	1.0984	1.6664	0.0513
2	0.0513	1.00044	1.3328	1.0983	1.1496	1.7368	0.0535
3	0.0535	1.00048	1.3327	1.0982	1.1517	1.7399	0.0536
4	0.0536	1.00048	1.3327	1.0982	1.1518	1.7400	0.0536

$$\therefore u_2 = 0.0536 .$$

Then, by (4),

$$H_2 = \frac{wx_2}{2u_2} = \frac{1.85 \times 60}{2 \times 0.0536} = 1034 .$$

Resisting force at extreme = 60,000/80 lb.$_w$ = 750 lb.$_w$.

$$\therefore H_3 = 1034 - 750 = 284 ,$$

$$u_3 = \frac{1.85 \times 60}{2 \times 284} = 0.1953 .$$

Then

$$\frac{\sinh u_2}{u_2} = 1.00048, \quad \frac{\sinh u_3}{u_3} = 1.00637 ,$$

$$\frac{\sinh u_1}{u_1} = 1 + \frac{0.00048 + 0.00637}{2} = 1.00343 ,$$

$$u_1 = 0.1434 ,$$

$$a = 0.00343 - 0.00048 = 0.00295 ,$$

$$80a = 0.236 .$$

Hence the sway at the 80 ft. level for extreme pressure is 0.236 ft. or 2.83 in.

To answer the second question, with the direction of external pressure bisecting the angle between the two planes of the cables each opposite pair of the cables would provide half the resisting force, that is, 375 lb.$_w$. Also, if the sway of the column were $80a$, then the sway in the planes of the cables would be $80a \cos 45°$.

Now if the parameters of an opposing pair of cables at extreme sway were u_2 and u_3, then

$$\frac{1.85 \times 60}{2} \left(\frac{1}{u_2} - \frac{1}{u_3} \right) = 375 ,$$

or

$$\frac{1}{u_2} - \frac{1}{u_3} = 6.76 .$$

One solves this equation by bracketing:

$$u_1 = 0.1434, \quad (\sinh u_1)/u_1 = 1.00343$$

$$(\sinh u_2)/u_2 = (\sinh u_1)/u_1 - a\cos 45°, \quad (\sinh u_3)/u_3 = (\sinh u_1)/u_1 + a\cos 45°.$$

$a\cos 45°$	$(\sinh u_2)/u_2$	$(\sinh u_3)/u_3$	u_2	u_3	$1/u_2$	$1/u_3$	$\frac{1}{u_2} - \frac{1}{u_3} - 6.76$
0.002	1.00143	1.00543	0.0927	0.1805	10.79	5.54	-1.51
							$\frac{15}{93} = 0.2$
0.003	1.00043	1.00643	0.0510	0.1963	19.61	5.09	$+7.76$
0.0022	1.00123	1.00563	0.0860	0.1837	11.63	5.46	-0.59
0.0023	1.00113	1.00573	0.0823	0.1853	12.15	5.40	-0.01
0.0024	1.00103	1.00583	0.0787	0.1868	12.71	5.37	$+0.58$

$$\therefore a\cos 45° = 0.00230\,.$$

Therefore the sway at the 80 ft. level is

$$80 \times 0.00230 \times 1.414 = 0.260 \text{ ft.} = 3.12 \text{ in.}$$

One might offhand think that the sway would be greater in the plane of two cables than in the direction which bisects the angle between the two planes, since all four cables are brought into play. The reason why the sway is greater in the second case than possibly anticipated is that the resistance is not a linear function of the sway, but builds up rapidly as the sway increases.

Further Principles of Application

1. Since

$$\sinh k' = \frac{y}{x_1} \div \frac{\sinh u_1}{u_1}\,,$$

and $(\sinh u_1)/u_1$ does not differ greatly from 1, then $wy^2/(8\sinh^2 k')$ is very nearly $wx_1^2/8$. Also, it has already been pointed out that when λ is large the second term of (20) is negligible. Therefore the absorption of energy is, to a close approximation,

$$\frac{wx_1^2}{8}\left[\frac{2u - \sinh 2u}{\sinh u}\right]_{u_1}^{u_2}.$$

Applied to the problem just solved the absorption of energy is, in the first case 44 ft. lb.$_w$, and in the second case 52 ft. lb.$_w$.

2. To find the sag of a cable below the chord joining its points of support it is better to use a different form of the equations (2, p. 247), viz.,

$$y = c\left\{\cosh\left(\frac{x}{c} + k\right) - \cosh k\right\},$$
$$\frac{dy}{dx} = \sinh\left(\frac{x}{c} + k\right), \tag{30}$$

for the c and k are the same for all segments of a given catenary, whereas the u and k' depend on the segment being considered.

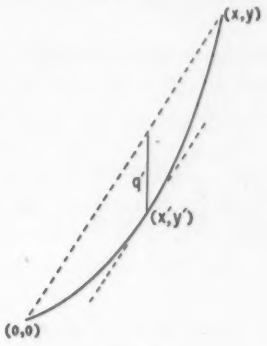

FIG. 2

The slope of the chord is y/x_1, and if (x', y') is the point where the tangent is parallel to the chord then

$$\sinh (x'/c + k) = y/x_1 , \tag{31}$$

and

$$q' = \frac{x'y}{x_1} - c \left\{ \cosh \left(\frac{x'}{c} + k \right) - \cosh k \right\} . \tag{32}$$

We also have

$$\frac{x_1}{2c} = u_1, \qquad \frac{x_1}{2c} + k = k'. \tag{33}$$

To find q' at the initial setting we then proceed as follows:

We are given x_1, y, and u_1.

From (6) find k'.

From (33) find c and k.

Then find x' from (31).

Substitute in (32) and obtain q'.

Proceeding thus in the problem just solved we have, for each cable at time of setting, the following results:

We start with $x_1 = 60$, $y = 80$, $u_1 = 0.1434$.

We then find in succession $k' = 1.096$, $c = 209$, $k = 0.953$, $x'/c + k = 1.0986$, $x' = 30.6$, $q' = 3.7$.

The sag of the cable below the chord is therefore 3.7 ft.

Summary

In any system of guy wires the behavior of the system depends on (1) the horizontal and vertical distances of the cable attachments from the foot of the column being supported, (2) the weight of the cable per unit length, and (3) the tension to which the cables are strung.

The conditions which have to be met are (1) a maximum allowable tension under extreme sway, (2) a maximum sway for a given lateral pressure on the column, and (3) a sufficient restoring moment when a given tension or sway has been experienced.

The methods here given enable one to design a system which will serve any specified purpose, or to determine the effectiveness of a given system when it is subject to a hypothetical strain.

References

1. CAMPBELL, J. W. Numerical tables. Douglas Printing Co., Edmonton. 1946.
2. CAMPBELL, J. W. An introduction to mechanics. Pitman Publishing Corporation, New York. 1947.

NOTES

Further Remarks on "Photometry and Colorimetry of Railroad Fusees"*

In a recent paper in this journal (1), the writer described a method for the colorimetry of railroad fusees with a trichromatic colorimeter, in which it was stated that the color of the fusees was always more saturated than the colors produced by mixing the light passing through Wratten filters No. 70 (Red) and No. 74 (Green). This result was later found to disagree with the results of a different method, and a search has been made for the cause of the discrepancy.

It has now been found that, at least for some observers, a match set up for a steady light of about the same chromaticity as a red fusee is entirely unsatisfactory if the light is then made to flicker at the rate of a few times per second (i.e., well below the critical frequency). The amount of blue in the mixture required for a match is then much less. The matter is receiving further study, but I wish now to point out that the numerical results represented by Fig. 8 of the paper are inexact. The other conclusions are not affected.

1. MIDDLETON, W. E. K. Can. J. Research, F, 26 : 331-339. 1948.

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